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Materials and technologies for SOFC-components

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Abstract

Solid oxide fuel cells are a forward looking technology for a highly efficient, environmental friendly power generation. A SOFC is a multilayer structure consisting of ceramic and metallic materials with different electrical transport properties. All components have to show a well adjusted thermal expansion behavior, chemical compatibility of material interfaces and chemical stability in the prevailing atmospheres. The performance of SOFC single cells is not only determined by intrinsic material properties. There is a significant influence due to the fabrication technology respectively the microstructure at the electrode/electrolyte-interfaces. The performance of cells can only be improved by the application of elevated materials using appropriate technologies. © 2001 Elsevier Science Ltd. All rights reserved.

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1. SOFC — areas of application

Solid oxide fuel cells are electrochemical energy converters which directly transform the chemical energy of a fuel gas into electrical energy. Due to the high operating temperature (700–1000°C) a wide variety of fuels can be processed. Within recent years substantial progress in materials and fabrication-technologies enabled field tests of SOFC-systems. Small stationary SOFC units in the power range of 1–100 kW are capable of electrical net efficiencies up to 50% [1–3] and overall efficiencies of about 70–90% (including thermal power) whereas larger pressurized SOFC/gas-turbine systems in the MW-range are expected to achieve electrical net efficiencies up to 70%.[4] Besides the stationary application of SOFC in small combined heat and power generation systems for single family houses, medium sized cogeneration units and large SOFC/GT power plants, mobile applications of SOFC attracting more interest within the last years. The development of SOFC-based auxiliary power units (APU) for cars, trucks (BMW/Delphi)[5] and military applications[6] as well as the development of low cost, high power density SOFC core modules which can be used in stationary as well as in a mobile systems (SECA: solid state energy conversion alliance) broadens the areas of SOFC-application and enhances the demands on SOFC-materials and components (Fig. 1).

Besides efficiency and power density additional requirements like long term stability, thermal cycling capability, short startup time and operation on different fuels at a high fuel utilization, have to be fulfilled. Table 1 gives an overview of the estimated targets for stationary and mobile SOFC systems.

The targets concerning power density and efficiency for stationary SOFC application can be fulfilled even at low operating temperatures (600–800°C),[7–9] whereas the properties of cells and stacks concerning long term stability (including thermal cycling), operation on different fuels and system costs have to be improved significantly within the next years.

2. SOFC — material requirements

The SOFC-stack is a multilayer structure consisting of ceramic and metallic materials. There are different types of SOFC concepts, basically tubular and planar ones which differ in the single cells design and arrangement, interconnector materials and gas flow. SOFC-stack materials have to fulfill different requirements. Electrolyte and interconnector have to be gas tight and

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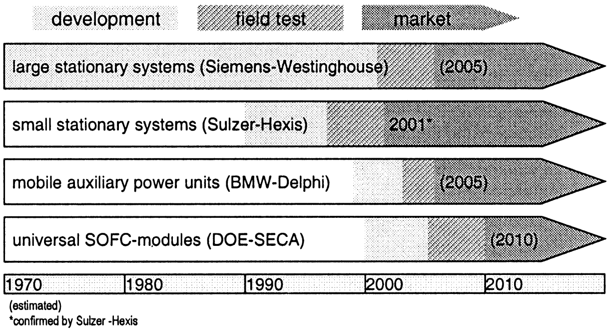

Fig. 1. Development status and targets for different SOFC applications.

Table 1
Target areas for mobile and stationary SOFC-systems

Application	Stationary	Mobile (traction)
Operation temperature		
Power density	> 0.25 W/cm^2	> 1 W/cm^{2a}
	700–1000°C	500–700°C
Lifetime (operation)	> 40,000 h	> 2000 h
Degradation rate	< 1 μV/h	< 10 μV/h^a
Fuel utilization	> 80%	> 80%^{a}
Thermal cycles	> 100^a	> 5000^a
Heating rates	> 1 K/min	> 100 K/min^a
Fuel	Natural gas, fuel oil	Gasoline, diesel
Oxidant	Air	Air
System costs	< \$500/kW	< \$100/kW

[a] Estimated numbers.

purely ionic resp. electronic conducting membranes whereas the electrodes have to enable the transport of electrons and of gaseous reactants and reaction products and therefore have to be porous. In case of a pure electronic conducting electrode material, the electrochemical reactions are restricted to the triple phase boundaries (tpb). The transport of oxide ions within the electrode material is advantageous concerning the number of possible reaction pathways. Therefore, electrodes should be a composite consisting of an electronic and an ionic conducting phase or a mixed conducting metal oxide to enlarge the active area into the electrode volume (Fig. 2).

The electrode materials should exhibit a high catalytic activity for the desired chemical and electrochemical reactions. The microstructure of the electrodes should display a large number of active reaction sites. All materials and components of the stack have to show chemical stability in the prevailing atmospheres whereupon changes in the gas composition due to fuel and oxygen utilization, fuel supply failures and leakage in the stack have to be taken into account. The compatibility in-between the different materials i.e. a well adjusted thermal expansion behavior, chemical compatibility and good adhesion at the interfaces has to be fulfilled.

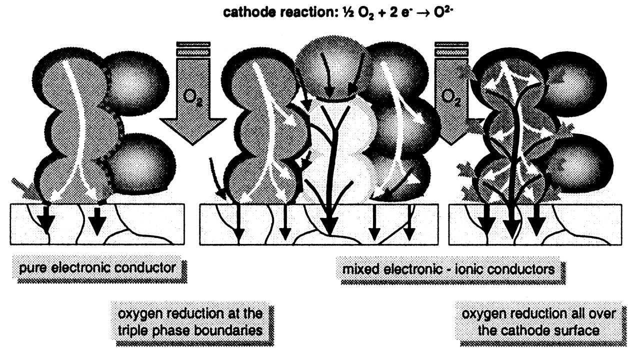

Fig. 2. Oxygen reduction at a pure electronic, composite and mixed conducting cathode.

State of the art materials currently used in most SOFC systems are yttria stabilized zirconia (YSZ) as the electrolyte, strontium doped lanthanum manganite (LSM) resp. a LSM/YSZ-composite as an electrochemical active layer as the cathode and nickel/YSZ-cermets as the anode (Fig. 3).

3. Materials and cells for reduced operating temperature

Depending on the SOFC concept, the operating temperature of a SOFC is restricted by different thermal activated processes like the oxide ion conductivity of the solid electrolyte and different chemical and electrochemical reaction steps in the electrodes or at the electrode/electrolyte interfaces. Decreasing the operating temperature generally results in increased losses resp. a decreased power density at a constant efficiency. On the other hand, the long term stability of the system is improved and the system costs can be reduced by using less costly metal alloys as interconnects and for external components. Therefore the development of alternative materials and components for SOFC-sytems operating economically at temperatures in-between 600 and 800°C or even below is necessary.[11] On the other hand it has to be taken into account that the operating temperature of a SOFC-stack is restricted by the system requirements as well as the fuel processing demands. In the case of a pressurized SOFC combined with a gas turbine, a very low operating temperature (~600°C) exhibits no benefits at all. To take advantage of internal reforming, SOFCs operating on different, disposable fuels like natural gas, fuel oil, gasoline or diesel require a minimum operating temperature depending on the composition of the fuel. For the state of the art SOFCs operating on natural gas an undermost operating temperature of about 650°C is necessary.

Fig. 4 shows the cell voltage and the losses of an electrolyte supported single cell i.e. an 8YSZ electrolyte substrate with screenprinted LSM cathode and Ni/YSZ cermet anode. This type of cell is able to operate in a temperature range from 1000 to 850°C whereas at lower temperatures the internal resistance is too large i.e. the efficiency or power density is not satisfying.

Using other types of solid electrolytes (Table 2) with a higher oxide ion conductivity (Fig. 5) is one possibility to increase the performance of single cells at reduced operating temperatures.

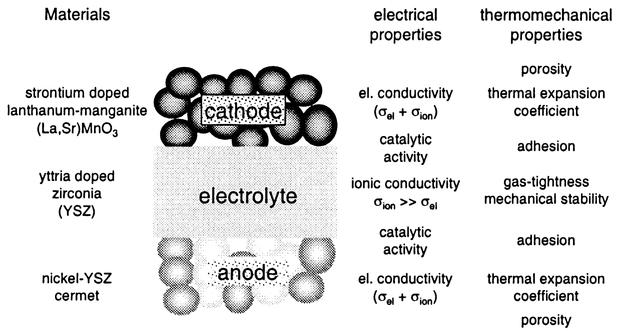

Fig. 3. State of the art materials and required electrical and (thermo-) mechanical properties of SOFC-single cells.

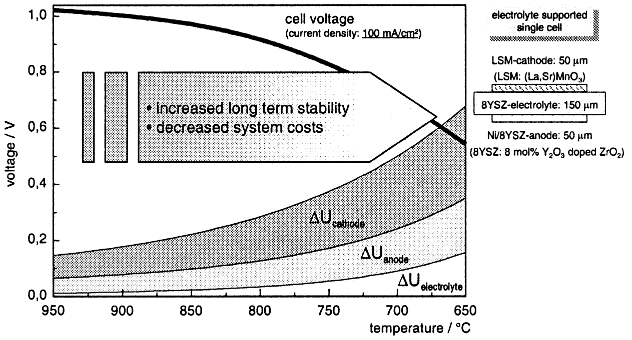

Fig. 4. Cell voltage of an electrolyte supported single cell (150 µm 8YSZ electrolyte substrate) at a constant current density of 100 mA/cm^2 as a function of operating temperature (the power density at 100 mA/cm^2 does not meet the requirements).

Yttria stabilized zirconia YSZ, the state of the art electrolyte material for SOFC so far, can be used either as TZP (3YSZ: ZrO$_2$ doped with ~3 mol% Y$_2$O$_3$) or CSZ (8YSZ: ZrO$_2$ doped with ~8 mol% Y$_2$O$_3$).[10] Although the oxide ion conductivity of TZP is significantly lower, this material is advantageous because of its outstanding mechanical stability.

Ce-based oxide ion conductors like Gd doped CeO$_2$ (GCO) offer a significantly higher ionic conductivity but they become mixed conductors in the anode environment resulting in an internal short circuit of the cell. Therefore, a decreased open circuit voltage (OCV) and an additional fuel utilization even under OCV-conditions takes place resulting in a decreased system efficiency (Fig. 6).

Lanthanum gallate (LSGM: (La,Sr)(Ga,Mg)O$_3$) based electrolytes exhibit an even higher ionic conductivity but the long term stability due to Ga-evaporation in a reducing atmosphere as well as the compatibility to Ni resp. NiO seems to be a severe problem at high operating temperatures. The use of LSGM-electrolyte-substrates contains problems due to the low mechanical stability of LSGM and the high costs of gallium.

Regarding all the requirements for an electrolyte material, it is still questionable if zirconia based materials can be replaced. Using scandium instead of yttrium as a dopant for zirconia is a possibility to increase the ionic conductivity significantly. Sc-doped ZrO$_2$ electrolytes are the most promising alternative for reduced operating temperatures so far.[12] But up to now the price and availability of scandium is uncertain and there is no high quality ScSZ-powder available yet.

Another possibility to decrease electrolyte losses is a reduction of the electrolyte thickness by using an electrode supported thin film electrolyte. Fig. 7 shows the voltage losses in the electrolyte at 300 mA/cm^2, an acceptable current density for SOFC's, as a function of temperature and electrolyte thickness.

Table 2
Advantages and disadvantages of possible electrolyte candidates for SOFC

YSZ	GCO	LSGM	ScSZ
•Excellent stability in oxidizing and reducing environment •Excellent mechanical stability (3YSZ) •> 40,000 h of fuel cell operation possible •High quality raw materials available	•Good compatibility with cathode materials •Mixed electronic-ionic conductor at low pO$_2$ (application in anode cermets)	•Good compatibility with cathode materials	•Excellent stability in oxidizing and reducing environment •Better long term stability than 8YSZ?
•Low ionic conductivity (especially 3YSZ) •Incompatible with some cathode materials	•Electronic conduction at low pO$_2$→low OCV •Mechanical stability	•Ga-evaporation at low pO$_2$ •Incompatable with NiO •Mechanical stability	•Availability and price of scandium

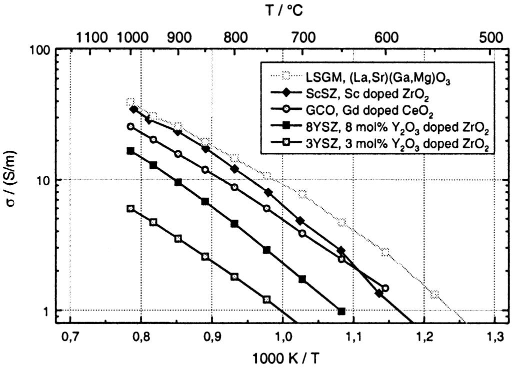

Fig. 5. Oxide ion conductivity of different electrolyte materials.[10,11]

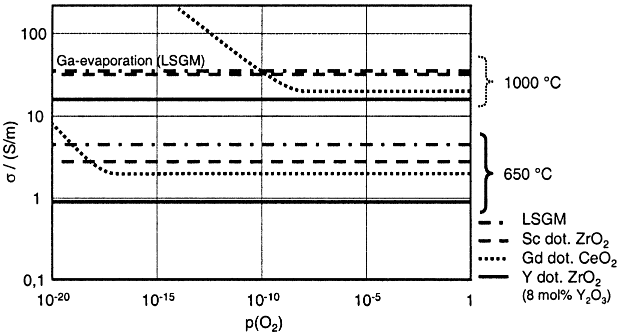

Fig. 6. Conductivity of different electrolyte materials as a function of oxygen partial pressure. In the case of Gd doped CeO2 an increase of the conductivity at low p(O2) occurs due to the formation of mobile electrons resulting in an internal short circuiting of the cell.

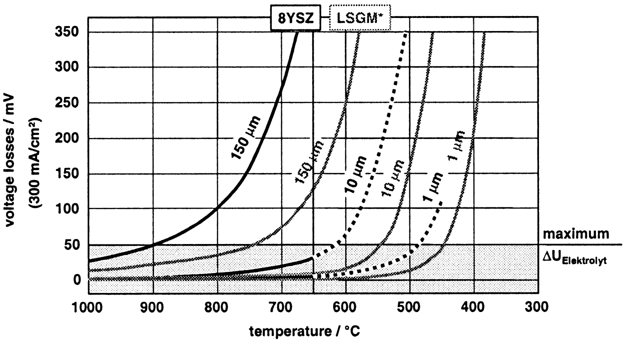

Fig. 7. Electrolyte losses as a function of operating temperature and electrolyte thickness for 8YSZ and LSGM (current constriction ignored).

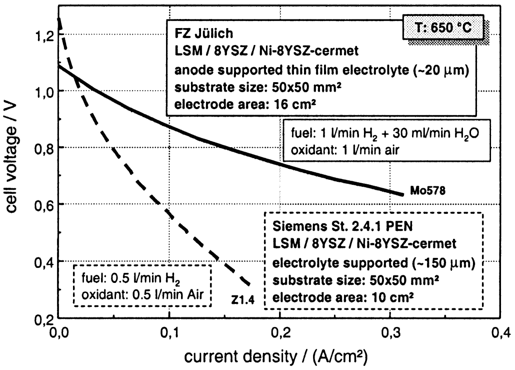

Fig. 8. Current/voltage characteristics of electrolyte and anode supported single cells consisting of state of the art materials (LSM/8YSZ/Ni-8YSZ) at 650°C.

Assuming that the electrolyte losses should not exceed 50 mV, the undermost operating temperature of electrolyte supported single cells (150 μm electrolyte thickness) is about 750°C whereas an electrode supported electrolyte theoretically exhibits an undermost operating temperature of less than 500°C. Including the polarization losses at the electrodes a sufficient cell performance can be achieved at about 650–750°C using the state of the art materials (Fig. 8).

To increase the cell performance at decreased operating temperatures, the polarization losses of the electrodes, mainly the cathode have to be decreased. On the one hand the electrochemical properties of the cathode can be influenced by choosing an appropriate composition. Lots of perovskite type as well as other oxides have been investigated with respect to their suitability as a cathode material. Many of them exhibited a composition like (La, Sr, Ca)(Cr, Mn, Fe, Co, Ni)O_3. One example is the $La_{0.8}Sr_{0.2}Mn_{1-x}Co_xO_3$ solid solution (LSMC). The electrical and oxygen ion conductivity of LSM can be increased significantly by substituting a part of the manganese with cobalt (Fig. 9).[13,14]

On the other hand, a high amount of cobalt results in an increased thermal expansion coefficient resulting in a delamination at the cathode/electrolyte interface resp. a cracking of the electrolyte. To solve this problem, either a composition with a small amount of cobalt or a composite consisting of lanthanum cobaltate and an appropriate amount of electrolyte material with a well adjusted thermal expansion behavior can be used. Another problem of LSMC-cathodes is the insufficient chemical compatibility between cobalt containing cathode materials and YSZ. During sintering of the cathode/electrolyte-interface, the formation of large amounts of secondary phases like lanthanum- and strontium-zirconate takes place, resulting in a significant increase of the polarization resistance (Fig. 10).[15]

4. SOFC under operating conditions

During operation different spatial and temporal gradients of temperature, gas composition and pressure occur in a SOFC-stack. A temperature gradient between gas inlet and outlet of about 100 K is a typical value which might even be increased due to the endothermic reforming reaction. Temperature gradients induce thermal stress within the stack and might cause cracking of the electrolyte or the sealant. The gradients result in an inhomogeneous distribution of the electrical and chemical potentials and the current density distribution in the cells. A dynamic operation i.e. a temporal variation of the electrical or thermal power output results in dynamic changes of the different types of gradients. Diffusion, electromigration and demixing within parts of the multilayer structure is significantly influenced by these gradients.

In the case of a state of the art Ni/YSZ-cermet anode a fine dispersed cermet microstructure is used to obtain a large number of active triple phase boundaries. During operation at high current density and fuel utilization a significant increase of the anode resistance occurs. Investigation of the microstructure after long term operation revealed, that an enhanced agglomeration of Ni takes place under current flow conditions at high fuel utilization (Fig. 11).[16] To prevent Ni-agglomeration in the anode, an optimization of the microstructure is necessary.

At the cathode/electrolyte-interface (LSM-cathode/YSZ-electrolyte) microstructural changes as well as demixing of the materials takes place in dependence of the operating conditions. The formation of micropores at the LSM/YSZ-interface takes place and an interdiffusion of manganese into the electrolyte can be observed.[17]

In the case of realistic operation including thermal cycling, the microstructural changes at the interface decrease the adhesion of the cathode layer on the electrolyte surface. Even a small number of thermocycles (~5) may result in a significant increase of the cathode resistance due to a partial delamination of the cathode layer (Fig. 12).

To increase the performance as well as the long term and thermocycling stability of the cathode/electrolyte interface, an accurate design of the materials, the interface microstructure and the production parameters is essential. To increase the cathode performance, the number of active reaction sites has to be increased. This may be achieved using a composite electrode consisting of a LSM/YSZ-composite. The disadvantage of a composite electrode is the arbitrary distribution of the LSM- and YSZ-particles. Therefore, only a part of the electrode volume is active for oxygen reduction. A well defined increase of the effective electrolyte surface area can be achieved by a structured electrolyte surface. Sintering single 8YSZ-particles onto the electrolyte substrate and covering the increased surface area by an electrochemical active thin film cathode via MOD (metal-organic-deposition) is a possibility to increase the number of active reaction sites significantly. An additional macroporous LSM-layer is used as a current

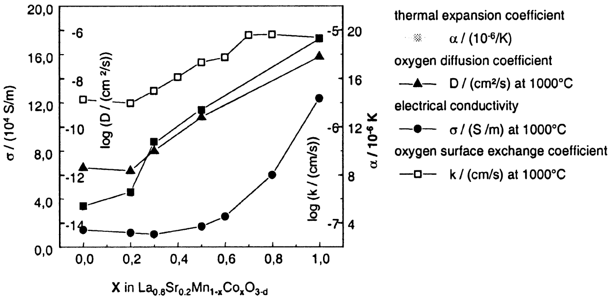

Fig. 9. Electrical and thermomechanical properties of the $La_{0.8}Sr_{0.2}Mn_{1-x}Co_xO_3$ solid solution.

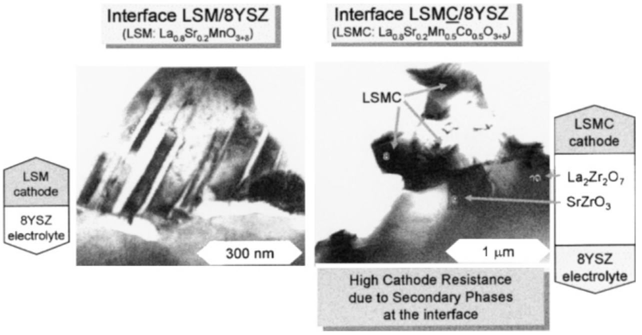

Fig. 10. TEM images of cathode/electrolyte-interfaces. The interface between LSM and 8YSZ shows a smooth transition between cathode and electrolyte whereas in-between the cobalt containing LSMC cathode and the 8YSZ electrolyte the formation of secondary phases (lanthanum- and strontium-zirconate) takes place.

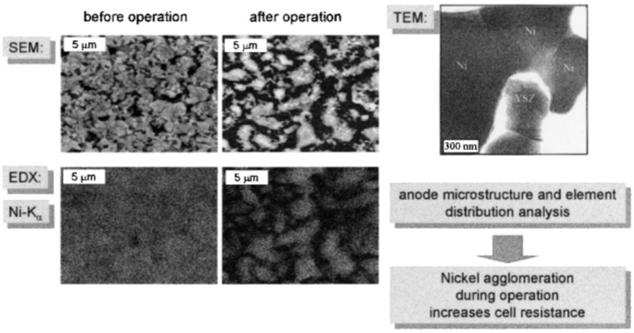

Fig. 11. Microstructural changes in Ni/YSZ-cermet anodes. During operation, the initially fine dispersed Ni-particles in the cermet form large Ni-agglomerates resulting in a decreased number of triple phase boundaries and an increased polarization resistance of the anode.

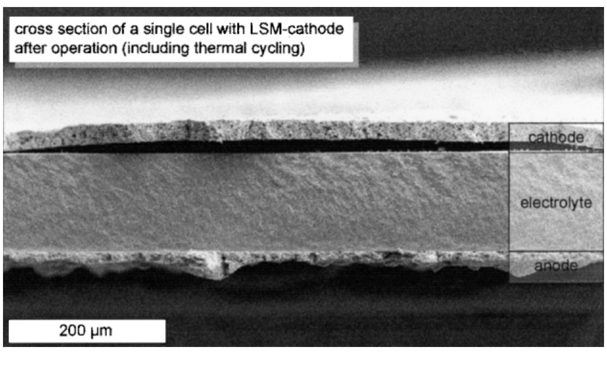

Fig. 12. Cathode delamination due to thermal cycling of a state of the art single cell.

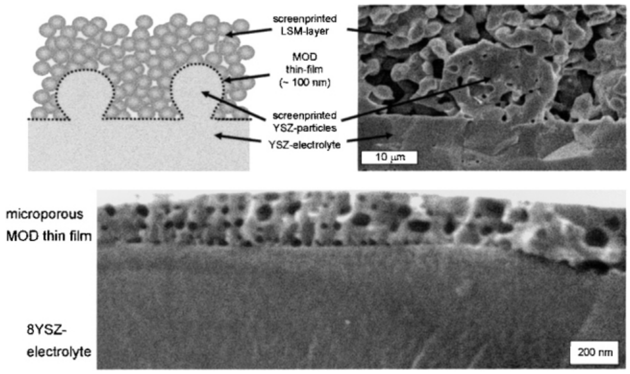

Fig. 13. Improvement of performance and long term stability of the cathode/electrolyte interface. The electrolyte surface is enlarged by applying single YSZ-particles. The enlarged surface is covered by a nanoporous LSM-MOD-thin film as an active cathode layer. An additional LSM-layer applied by screenprinting.

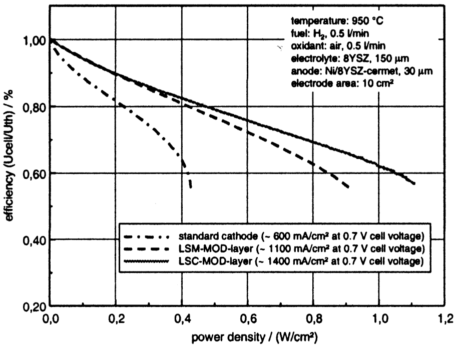

Fig. 14. Efficiency vs. power-density of single cells with different types of cathode.

collecting and gas distribution layer. The adhesion of the cathode is improved due to the 3-dimensional penetration structure (Fig. 13).

Beneath a significant increase in power density, the long term and thermal cycling stability is increased. The thin film cathodes showed no severe delamination at all.[18] Due to the low processing temperatures for the thin film cathode, the use of a mixed conducting LSC-thin film (LSC: (La, Sr)CoO_3) is possible. These cathodes showed an even higher performance (Fig. 14), without degradation during an operation time of more than 1000 h.

5. Conclusions

Solid electrolyte materials have to be stable over a wide range of oxygen partial pressures and temperatures. Candidate materials for medium and low temperature operation (800–500°C) have to be examined for invariant chemical composition and crystal structure as well as for mechanical stability and electrical properties. Yttria doped zirconia in the cubic (YSZ) and in the tetragonal (TZP) structure are still the most promising materials, scandia doped zirconia has to be taken into account as an alternative material. Electrode materials have to be well adjusted to the chosen electrolyte material in terms of chemical compatibility, thermal expansion coefficient and microstructure properties. The next generation of SOFC single cells will consist of thin film electrolytes for low temperature operation and custom tailored electrode/electrolyte interfaces for long term stability and high efficiency. All cell components have to be developed with adequate mechanical properties for thermal cycling and fast light off.

Acknowledgements

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