

Advances, aging mechanisms and lifetime in solid-oxide fuel cells

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Abstract

Solid-oxide fuel cells (SOFCs) are an energy conversion device that theoretically has the capability of producing electrical energy for as long as the fuel and oxidant are supplied to the electrodes but performance is expected for, at least, 40,000 h. In reality, performance degradation is observed in planar SOFC with metallic bipolar plate under steady and repeated thermal cycling conditions, which limits the practical operating life of these SOFCs. In this paper, the advances in SOFC are briefly summarized and the aging mechanisms of some components (anode, cathode and interconnect) in SOFC are discussed. The emphasis is given to aging mechanisms due to instability of materials and microstructures under real operation conditions. Identification of aging kinetics contributes to improvement in the stability of SOFC. It is indicated that development of new materials, optimization of microstructures and lower operating temperatures are desirable for the long-term stability of SOFC. Beneficial operation condition of SOFC is also proposed.

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Keywords: Solid-oxide fuel cell; Reduced temperature SOFC; Hydrocarbon fuels; Aging mechanism of components; Operation condition

1. Introduction

A fuel cell is an energy conversion device that generates electricity and heat by electrochemically combining a gaseous fuel and an oxidizing gas via an ion-conducting electrolyte. The chief characteristic of a fuel cell is its ability to convert chemical energy directly into electrical energy without the need for combustion, giving much higher conversion efficiencies than most conventional thermo-mechanical methods (e.g., steam turbines). Consequently fuel cells have much lower carbon dioxide emissions than fossil fuel-based technologies for the same power output. They also produce negligible emissions of NO_x, the main constituents of acid rain and photochemical smog. As with other technologies, it is very important to achieve a service life of several thousand hours without impacting performance levels. Several types of fuel cells are now being developed around the world, the chief difference between them being the material used for the electrolyte (and thus also their operating temperature).

Solid-oxide fuel cells (SOFCs) consist entirely of solid-state materials; they utilize a fast oxygen ion conducting ceramic as the electrolyte, and operate in the temperature range of 700–1000 °C.

SOFCs have several features that make them more attractive than most other types of fuel cells:

- The highest efficiencies of all fuel cells (50–60%);
- A potential long-life expectancy of more than 40,000–80,000 h;
- Constructed from readily obtainable ceramic materials, not precious metals like platinum;
- Few problems with electrolyte management (cf. liquid electrolytes, which are typically corrosive and difficult to handle);
- High-grade waste heat is produced, for combined heat and power (CHP) applications increasing overall efficiencies to over 80%; and
- Internal reforming of hydrocarbon fuels is possible.

SOFC systems are being advanced by a number of companies and organizations with three major fuel cell stack designs emerging. The major design types are tubular, planar, and monolithic. Only the first two are currently being developed. Tubular SOFC designs are closer to commercialization and are being mainly produced by Siemens Westinghouse Power Corporation (SWPC). The tubular SOFC design constructs the stack as a bundle of tubular electrode–electrolyte assemblies. Air is typically introduced to the inside of each tube while fuel bathes the outside of the tubes to produce electricity. One distinct feature of this design is that it has no seals. Demonstrations of tubular SOFC technology have produced as much as 220 kW. Compared to tubular designs, planar SOFC designs consist of flat plates bonded together to form the electrode–electrolyte assemblies. This is a compact stack design. Individual cells can be electrolyte

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self-supporting or anode supported. The planar SOFC requires high-temperature gas seals at the edges of the plates. The planar designs have been demonstrated in single cell and smaller stack sizes in the single to multiple kilowatt range. In comparison with tubular SOFC, the planar SOFC could have the following advantages:

- Higher power densities, and better overall performance;
- Manufacturing process relatively simple and high potential for low cost manufacturing;
- Operating temperature below 800 °C possible; and
- High efficiency.

2. Advances in SOFC research and development

SOFC is emerging as a potential breakthrough technology for the low cost production of electricity. The low product cost is a prerequisite for the successful market introduction and penetration of SOFC power plants. SOFC has the advantage of fuel flexibility. Hydrogen is currently expensive to produce and deliver. Therefore, hydrocarbon fuels are a realistic choice in the immediate future for SOFC. In recent years, significant advances have been achieved in SOFC research and development, although a number of problems still have to be solved. The research and development is necessary to decrease capital costs, as well as to avoid the use of hydrogen as the primary fuel. Main recent advances in SOFC include realization of SOFC operating at temperature <800 °C and direct supply of hydrocarbon fuels.

2.1. SOFC operating at temperature <800 °C

Conventional high-temperature SOFC operates at around 950 °C. This temperature implies high material costs, particularly for interconnect and construction materials. In high-temperature SOFC, the interconnect may be a ceramic such as lanthanum chromite, or a sophisticated refractory alloy, e.g., based on mechanically alloyed Y/Cr. In either case, the interconnect represents a major proportion of the cost of the stack. Operation of the SOFC at a reduced temperature can overcome some of these problems and bring additional benefits.

Advantages of SOFC at $T < 800$ °C:

- Low cost metallic materials, e.g., ferritic stainless steels can be used as interconnect and construction materials. This makes both the stack and balance of plant cheaper and more robust (balance of plant is widely assumed to constitute 50% of the cost of the SOFC system).
- Potential for rapid start up and high capability of thermal cycle.
- Simplification of the design and materials requirements of the balance of plant.
- Significant reduction of corrosion rates, higher long-term stability of the system.

As the operating temperature of the SOFC is reduced, the ionic conductivity of the electrolyte decreases, which results in a rapid deterioration of the performance of the SOFC. There are two ways of minimizing ohmic losses across the electrolyte at temperature <800 °C. One way is to use higher conductivity materials (doped ceria and lanthanum gallate). However, this will result in uncertainties of long-term stability and material compatibility. Another way is to use thin YSZ electrolyte membranes (5–50 μm). For SOFC application, it is desirable that the oxygen fluxes through YSZ electrolyte membranes attain values around 1 A cm⁻², and so with typical values of the electric potentials in the range 0.5–1.0 V. It follows that the area-specific resistance (ASR) term should be as low as possible. Adopting a typical target value of 0.15 Ω cm² enables the membrane thickness at different temperatures to be determined from Fig. 1 [1]. As shown in Fig. 1, the thin YSZ electrolyte membranes can work at temperatures 600–800 °C. When the electrolyte thickness is reduced from ~150 to ~5 μm, the resistance is decreased by more than one order of magnitude across the electrolyte.

Conventionally, planar cells use the electrolyte to support thin electrodes on either face. This limits minimum electrolyte thickness to around 150 μm. By using a thick, structural anode as the substrate, the mechanical stability of the cells is transferred from the electrolyte to the anode. Reduction of the YSZ electrolyte thickness can be achieved in a number of ways. If electrodes with optimized microstructure are used, electrochemical experiments show that at temperatures 600–800 °C it is easy to meet a minimum requirement of 0.2 W/cm² at an operating voltage of 0.7 V with anode as support. Fig. 2 shows the two kinds of cell concept.

A concerted effort is also being made by researchers around the globe to develop this substrate technology [2]. The most advanced development in this field is currently located at the Research Center Jülich in Germany and at Global Thermoelectric, Canada, whose technique is based on the Jülich concept. The Research Center Jülich works on the construction of SOFC stacks using the substrate cell technique. The design of these stacks is optimized with the aid of model calculations of temperature distribution, gas stream and mechanical load. The thermo-mechanical data required for these calculations are determined experimentally. Since a stack does not only consist of single cells but also of other components such as interconnect foils, contact layers and glass ceramic sealings, materials research plays an essential role. Another priority is stack construction. Within the technology development program on anode supported SOFC in Jülich short-stack (two cells 10 cm × 10 cm; 81 cm²) tests were performed in order to improve, among others, the durability [3]. First results with interconnect plates machined from a newly developed ferritic steel JS-3 show degradation rates less than 1%/1000 h during the first thousand hours of continuous operation. Several kW-class stacks (10–40 cells 20 cm × 20 cm; 361 cm²) were assembled and operated. The 40-cell stack produced a maximum power of

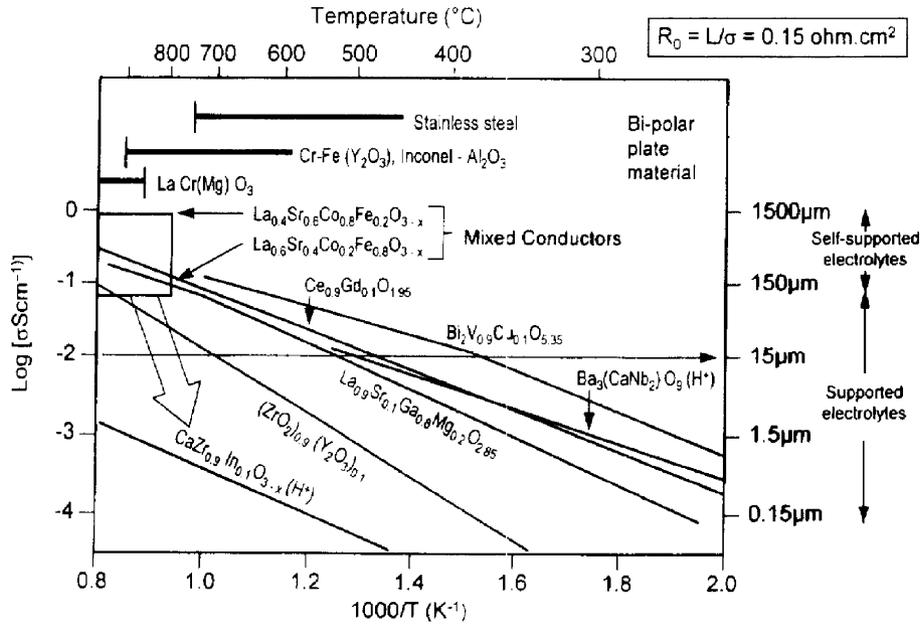


Fig. 1. Specific ionic conductivity values for selected ceramic oxide ion conducting membranes as a function of reciprocal temperature [1].

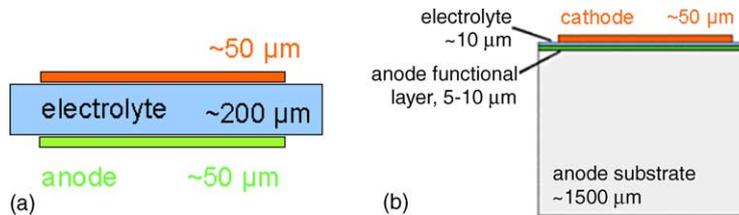


Fig. 2. The two kinds of cell concept: Conventional planar cell concept with self-supporting electrolyte (a) and Jülich membrane-electrode assembly (MEA) concept with the anode as the cell support (b).

9.2 kW (300 A at 30.2 V) operating on hydrogen (10% humidified, 76% fuel utilization). Operating on simulated partially pre-reformed methane the stack produced a maximum power of 5.4 kW (182 A at 30.2 V). A medium-term goal at Research Center Jülich is the design and construction of a 25 kW system for combined heat and power generation with natural gas in order to demonstrate the feasibility of an anode-substrate-based SOFC.

2.2. Direct supply of hydrocarbon fuels

One of the main attractions of SOFC over other types of fuel cells is their ability to handle more convenient hydrocarbon fuels—other types of fuel cell have to rely on a clean supply of hydrogen for their operation. Hydrogen derived from renewable resources would be an appropriate fuel. However, its availability and distribution are very limited. In the short to medium term future, the only realistic fuels are hydrocarbon based, especially natural gas. Because SOFCs operate at high-temperature there is the opportunity to reform hydrocarbons within the system either indirectly in a discrete reformer or directly on the anode of the cell.

A further process, direct oxidation can also occur at low steam partial pressures. This process offers the ultimate in thermodynamic efficiency, almost 100% theoretically.

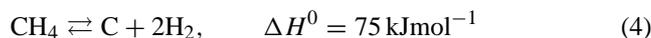
2.2.1. Reforming

Reforming enables SOFC to use hydrocarbon directly as fuel. The reaction Eq. (1) for steam reforming can be formulated for methane as the main component of natural gas, which is generally associated with a water gas shift equilibrium reaction (2). Additionally, methane may be reformed with CO₂ (Eq. (3))



Two approaches have been developed, external and internal reforming. In the first case, the reaction occurs in a separate reactor, which consists of heated tubes filled with nickel or noble metal. In internal reforming, natural gas reforming can be directly carried out at the anode of the fuel

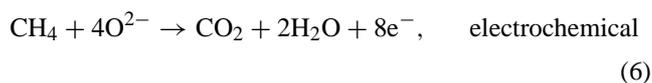
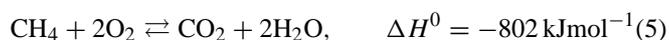
cell. Advantages of internal reforming over external reforming are the good and direct heat transfer between fuel cell stack and reforming zone and the high degree of chemical integration. Steam as a product of the electrochemical reaction in the cell can be directly coupled in as a base product of the reforming reaction, so that less steam for reforming must be produced in comparison with external reforming, improving the electrical efficiency. Other advantages include reduced system costs, more homogeneous hydrogen formation and higher methane conversion rate. However, as to the state-of-the-art anode Ni/YSZ, two major problems occur: the risk of carbon deposition and the creation of temperature gradients. Firstly, when insufficient steam is present, carbon may be deposited according to reaction (4),



which deactivates the anode. This cracking reaction is even more problematic with higher hydrocarbons, which also are present in natural gas. Therefore, a steam/methane ratio >2 is required to avoid carbon deposition. Secondly, high-temperature gradients arise in the region of the fuel inlet due to the significant cooling effect of the reforming process, which is on account of its very fast reaction rate in comparison to electrochemical reaction rate. This leads to strong thermal stressing of the materials of the fuel cell. Research efforts were made towards overcoming these problems. Some new materials were proposed to decrease the catalytic activity of Ni for reforming, in order to avoid carbon deposition without using excess steam. For example, the influence of adding iron to the Ni/YSZ cermet has been studied [4]. The iron achieves a decrease of the catalytic activity of nickel and adjusts the thermal expansion coefficient closer to YSZ. Furthermore, a new concept ‘gradual internal methane reforming’ has been proposed [5]. It is based on a local coupling between the steam reforming and the electrochemical oxidation of hydrogen. Thus, the reaction is distributed over the entire anode surface.

2.2.2. Direct oxidation

Direct oxidation of methane, reaction (5) has the thermodynamic possibility of 99.2% conversion efficiency. Operating fuel cells directly on hydrocarbons would obviously eliminate the need for reformer and improve efficiency. If this reaction is to be achieved, it is necessary to avoid or inhibit methane cracking. There is also considerable controversy as to whether the reaction is actually a direct anode oxidation of methane (Eq. (6)) or a reaction by a steam reforming process (Eq. (1)) including some intermediate reactions. The steam reforming process is associated with a water gas shift reaction (2). The produced H_2 and CO are then electrochemically converted to H_2O (Eq. (7)) and CO_2 (Eq. (8)), respectively. Therefore, the anode reaction of methane by a steam reforming process also leads to the net result shown in reaction (6).



There have been some successes reported for direct electrochemical oxidation with ceria-based materials. Firstly, Perry Murray et al. [6] reported the direct electrochemical oxidation of methane in SOFCs by using ceria/nickel composite electrodes at lower temperatures, $<700^\circ\text{C}$, i.e., at temperatures below the cracking of the hydrocarbon. The SOFCs were fabricated on porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) cathodes. The LSM pellets were ~ 2 cm in diameter and 1 mm thick, and were produced using standard ceramic processing techniques. All SOFC layers, starting with a 0.5-mm thick $(\text{Y}_2\text{O}_3)_{0.15}(\text{CeO}_2)_{0.85}$ (YDC) porous film, were deposited on the LSM pellet using d.c. reactive magnetron sputtering. The electrolyte, 8 mol% Y_2O_3 -stabilized ZrO_2 (YSZ), was then deposited under conditions yielding a dense, 8- μm thick film. To complete the cell, another 0.5- μm thick YDC film was deposited, followed by a porous, 2- μm thick Ni-YSZ anode. Fig. 3 shows measurements of current density and power density versus voltage, performed on a typical cell using air and methane. The results for dry and wet (with 3% H_2O) methane were nearly identical. Cell performance was stable in preliminary 100 h life tests, except for wet methane at low voltages where the anode Ni gradually oxidized. The results in Fig. 3 are similar to those obtained for the same cells operated with humidified hydrogen fuel, except that the power densities are $\sim 20\%$ lower. Examination of the anodes after the cell tests (by visual observation, energy dispersive X-ray, and scanning electron microscopy) showed no evidence of carbon deposition after ~ 100 h of operation.

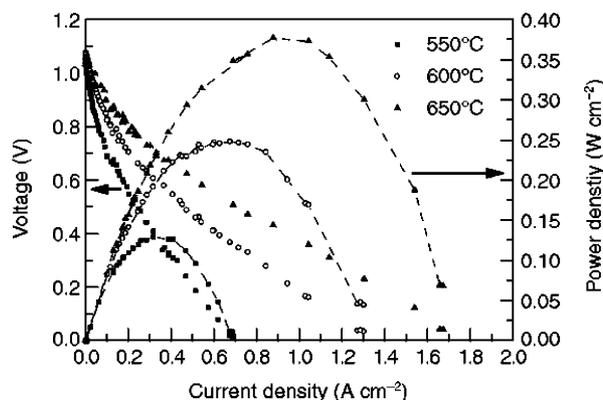


Fig. 3. Cell voltage and power density versus current density for an SOFC operated on air and wet methane. The measurements were collected in atmospheric-pressure air, and the methane fuel was supplied at $\sim 50 \text{ cm}^3 \text{ STP min}^{-1}$ [6] (reprinted by permission from Nature, 12 August, vol. 400, p. 649, copyright 1999, Macmillan).

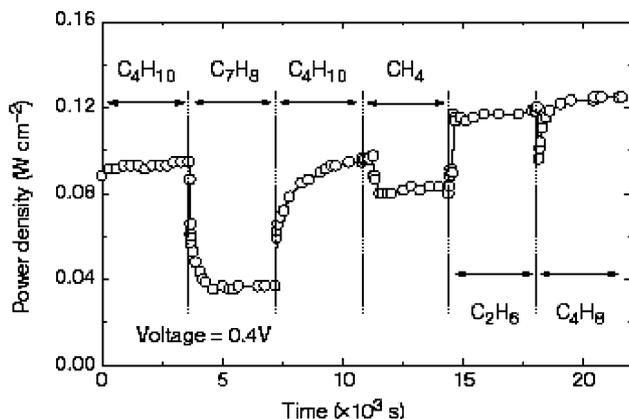


Fig. 4. Effect of switching fuel type on the cell with the Cu-(doped ceria) anode at 700 °C. The power density is shown as a function of time. The fuels were: *n*-butane (C₄H₁₀), toluene (C₇H₈), *n*-butane, methane (CH₄), ethane (C₂H₆), and 1-butene (C₄H₈) [7] (reprinted by permission from Nature, 16 March, vol. 404, p. 265, copyright 2000, Macmillan).

Secondly, Gorte and co-workers [7] report the direct, electrochemical oxidation of various hydrocarbons (methane, ethane, 1-butene, *n*-butane, and toluene) using a solid-oxide fuel cell at 700 and 800 °C with a composite anode of copper and ceria (or samaria-doped ceria). The SOFCs used here were prepared with a 60- μ m thick, YSZ electrolyte, 12.5 mm in diameter, and a cathode formed from a 50:50 mixture of YSZ and La_{0.8}Sr_{0.2}MnO₃ powders. The anodes were 40 wt.% Cu and 20 wt.% CeO₂, held in place by a YSZ matrix formed from zircon fibres. In a second cell, a 20% Sm₂O₃–80% CeO₂ mixed oxide replaced CeO₂. The first cell was operated at the maximum power density of 0.12 W cm⁻² in dry butane at 700 °C for a period of 48 h with no observable change in performance. Visual inspection of a cell after 2 days in *n*-butane at 800 °C showed that the anode itself remained free of the carbon deposits. The data in Fig. 4 show further improvements in cell performance of the second cell. For these experiments, the current densities were measured at a potential of 0.4 V at 700 °C. The power densities for H₂ and *n*-butane in this particular cell were approximately 20% lower than for the first cell, which is within the range of the ability to reproduce cells. However, the power densities achieved for some other fuels were significantly higher. In particular, stable power generation was now observed for toluene. Similarly, Fig. 4 shows that methane, ethane and 1-butene could be used as fuels to produce electrical energy. The data show transients for some of the fuels, which are at least partially due to switching.

3. Aging mechanism of components in SOFC

The commercial requirements for SOFC systems include a cell and stack life in the order of 40–50,000 h with very small degradation rates. All resistive limitations in an SOFC

may suffer from degradation. Demonstration of total stack durability is of primary interest, but an analysis of aging mechanism in each component is desirable. It is therefore essential to increase the understanding of the degradation of each component in SOFC.

3.1. Aging mechanism of anode

State-of-the-art SOFC anodes consist of a Ni-YSZ cermet. While Ni plays the role of the catalytically active as well as of the electronically conducting phase, the YSZ is added in order to support the Ni particles, to inhibit coarsening of the Ni, and to provide a thermal expansion coefficient which is similar to that of the zirconia based electrolyte. A homogeneous or graded structure consisting of three phases, Ni, yttria-stabilized zirconia (YSZ), and porosity, should be obtained, providing percolation paths for electrons, oxide ions, and gaseous hydrogen and water, respectively. This requirement originates in the poor conductivity of electrons in YSZ and oxide ions in Ni. The line where the three phases meet is referred to as the triple phase boundary (TPB) and is considered to be electrochemically active only if percolation paths for the active species are provided. The reaction rate for electrochemical oxidation of hydrogen has been demonstrated to correlate with the length of the TPB. In the research and development of SOFCs, serious reductions in cell performance have been observed due to degradation of the anode. The polarization characteristics of the anode are highly dependent on its morphology. The apparent activation energy has a distinct tendency towards lower value for fine cermets than that for coarse cermets [8]. It is widely accepted that sintering of nickel plays an important role [9]. The SOFC anode cermet is commonly made from YSZ and NiO powders. The NiO is then reduced in situ to nickel metal when exposed to the fuel in the fuel cell. Since nickel particles are high-surface-area solids, there will always be a thermodynamically driving force to decrease free energy, i.e., to minimize surface area. Thus, the sintering behavior of the nickel/YSZ anode is strongly dependent on the wetting properties of the nickel on the YSZ. The agglomeration of Ni particles under SOFC operating conditions leads a reduction in electrochemical reaction sites, namely TPB, and the cutting-off on current paths [10]. Fig. 5 shows, as an example, the effect of nickel sintering on the polarization of the anode [11]. Furthermore, shrinkage of the electrode upon firing also leads to decrease in the gas permeability of the electrode layer, the occurrence of shear stresses at the electrode–electrolyte interfaces, and increases in contact resistance between the electrode and the current collector when assembled as a stack.

There are a number of programs dedicated to long-term stability studies and the prevention of Ni agglomeration at the operating conditions of the fuel cell. In this regard, a novel anode microstructure has been proposed [12]. A feature of this new anode is that, unlike other materials, the YSZ powders are divided into coarse and fine particles. Upon

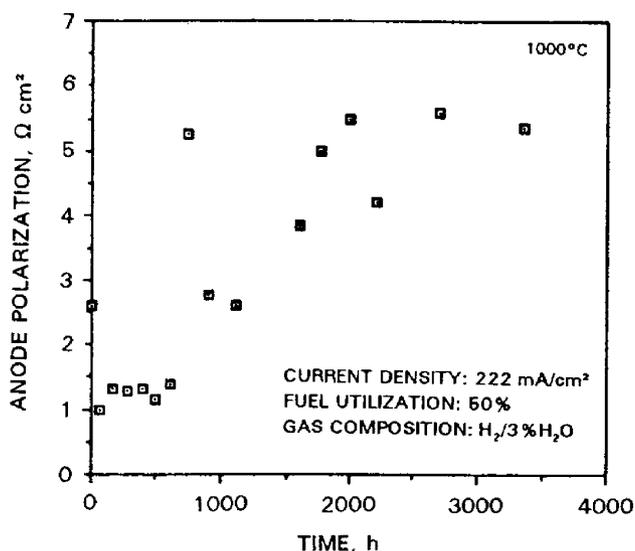


Fig. 5. Effect of nickel sintering on cermet anode polarization [11] (reproduced by permission of The Electrochemical Society).

sintering, the coarse YSZ particles are connected by a network of fine YSZ particles. This forms a strong framework, which prevents the agglomeration and coarsening of Ni particles. The shrinkage and porosity behavior for both sintering under reducing atmosphere at 1000 °C (as operating condition) and in air at 1400 °C (as producing condition) were measured and compared. The previous material showed considerable shrinkage and a large decline in porosity. On the other hand, the new material showed little shrinkage under producing condition and virtually no change in volume and porosity under operating condition. Fig. 6 shows the overpotentials for the two anodes during a long-term operation. The overpotential of previous anode rapidly rises after a few tens of hours, whereas the new one keeps the overpotential constant, allowing more 2500 h of continuous generation, which indicates superior long-term stability. Therefore, the durability of the anodes can be expected with optimization of the cermet structure.

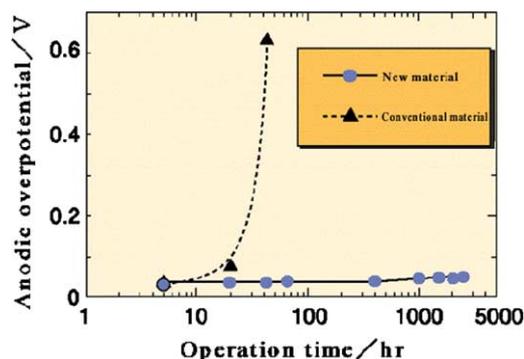


Fig. 6. Change in anodic polarizations between the previous and the new anodes at 0.2 A/cm² as a function of cell operating time [12] (reproduced by permission of Central Research Institute of Electric Power Industry, Japan).

3.2. Aging mechanism of cathode

A composite of A-site-deficient strontium-doped lanthanum manganite (LSM) and the electrolyte material, yttria-stabilized zirconia [13,14] is presently used as cathode in SOFC. The formation of low-conductive reaction products such as lanthanum zirconate at the cathode–electrolyte interface can be avoided during cell fabrication. Furthermore, the electrochemically active reaction zone may be extended from the interface between the electrode and the electrolyte to the bulk of the electrode. The cathode reaction depends on the catalytic activity and microstructure of composite cathodes. Cathode overpotential is often the main factor limiting SOFC performance. An attempt has been made to investigate whether temperature, current load or kinetic processes are responsible for the degradation [15]. The cathodes were kept at constant, realistic operating conditions (-300 mA cm^{-2} at 1000 °C in air) for up to 2000 h. Nominally identical cathodes are kept for 2000 h at 1000 °C in air without current load for comparison. After 2000 h test, the increase in electrode overvoltage exceeded 100% of the initial value for the electrodes with the galvanostatic load. However, the electrode without load showed little or no degradation. The pore formation, observed after the galvanostatic durability test, was a common feature for all the cathodes investigated. Fig. 7 shows the pore formation at the composite electrode layer (C-layer) interfaces, which might have caused a decrease in the length of active triple phase boundary between electrode, electrolyte and gas phase, as the contact area between composite electrode layer and electrolyte was decreased considerably.

As the polarization resistance scales with the inverse of TPB length, the microstructural changes might be responsible for the observed increase in polarization resistance during galvanostatic tests. When exposing a cation-deficient oxide material to an oxygen potential gradient cations can migrate towards the higher oxygen potential interface, while vacancies move in the opposite direction. This may lead to pore formation and pore movement [16]. The pores will preferably form at the interface with the lowest oxygen potential in places, where there is an indentation or a notch, as this part of the interface is unstable. The pores are transported towards the interface with the highest oxygen potential. The applied current creates an oxygen potential difference across the composite electrode layer and this difference may be the driving force of the pore formation.

The decrease in operation temperature of SOFC seems to assure the stability of cathodes [17]. The planar SOFC in Siemens design is made of cells or membrane–electrode assemblies (MEAs) connected in parallel or/and in series to a stack. MEA consists of planar solid electrolyte YSZ with a thickness of 150 μm and of two porous electrodes: cathode and anode. The cathode consists of two layers: electrochemically active layer from $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$ and YSZ composite and electronic conductive $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$ layer. After 5000 h of stack operation at 850 °C, 300 mA cm⁻² in Air/H₂,

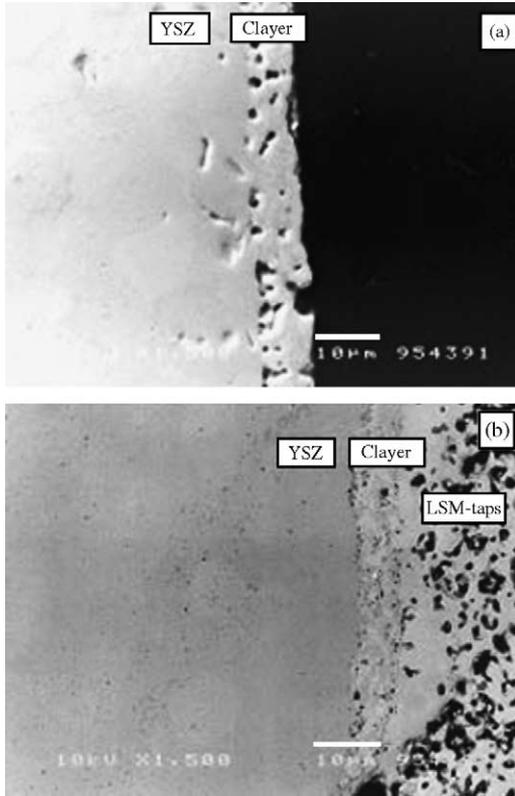


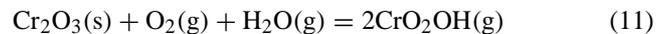
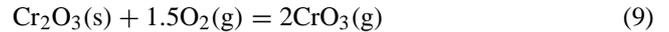
Fig. 7. Structural change in the composite cathode during operation at 1000 °C, 300 mA cm⁻² in air: reference sample (a) and after 2000 h with current load (b) [15] (reproduced with kind permission of Kluwer Academic Publishers).

no changes in the porosity of both layers were found. It means that no post-sintering takes place at 850 °C. The cross section of the cathode at initial state and after 5000 h of operation is shown in Fig. 8.

3.3. Aging mechanism of interconnect

Interconnect is one of the key components in planar SOFC, which provide the electrical connection between the

individual cells in a series to make SOFC stacks and separate the anode and the cathode gases. There are two types of interconnect materials commonly used in SOFC, doped LaCrO₃-based ceramic materials and high-temperature oxidation resistant alloy. The latter is more attractive because doped LaCrO₃-based ceramic materials have low mechanical strength and high manufacturing costs. The alloys used as metallic interconnects contain Cr in order to render possible formation of a chromia scale for corrosion protection. Novel Cr-based alloys are, for example, the oxide dispersion strengthened (ODS) alloy Cr5Fe1Y₂O₃. However, the use of chromium containing alloys can lead to a rapid degradation of the electrical properties of an SOFC due to chromium evaporation at the cathode side of the fuel cell [18]. The alloys form Cr₂O₃ under cathodic conditions. A thin layer of this oxide grows on the surface of the alloy. The oxide completely covers the alloy surface and determines the chromium vaporization. Depending on temperature and the partial pressures of H₂O and O₂, volatile chromium species are formed by the Cr₂O₃ layer:



The high valent oxides and oxyhydroxides of chromium in the vapor phase can also undergo cathodic reduction. Then oxide ions are formed which react subsequently with the fuel at the anode side as is the case in the reduction of oxygen. The electrochemical reactions involved in the reduction of CrO₂(OH)₂(g) are given as an example in detail.

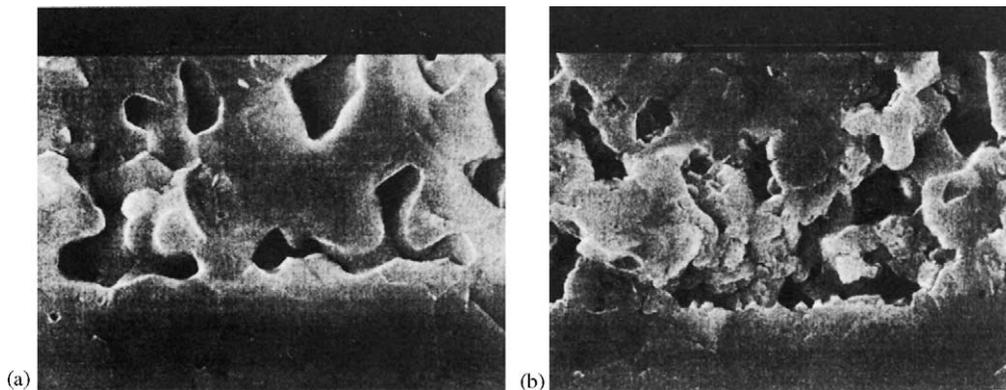
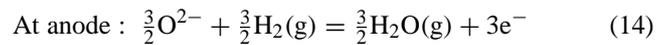
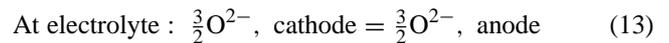
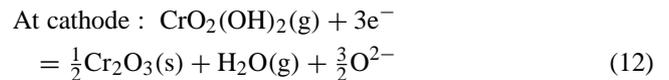
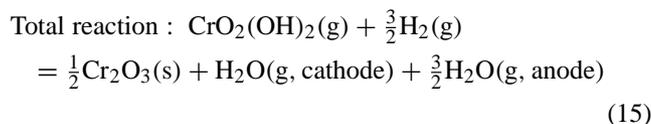
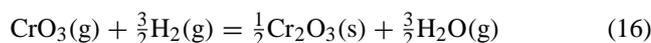


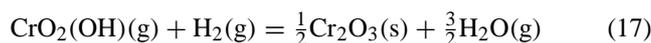
Fig. 8. Structural stability in the composite cathode during operation at 850 °C, 300 mA cm⁻² in air: Initial state (a) and after operation of 5000 h (b) [17] (reproduced by permission of European Fuel Cell Forum).



The following reactions for the overall cell result in the case of the involvement of $\text{CrO}_3(\text{g})$ and $\text{CrO}_2(\text{OH})(\text{g})$ in the cathodic reduction:

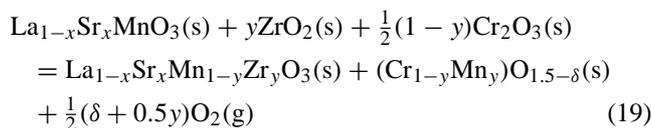
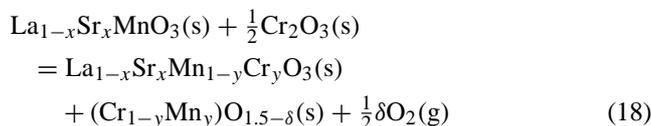


and



The result of such processes is the precipitation of $\text{Cr}_2\text{O}_3(\text{s})$ phase at the cathode–electrolyte phase boundary. The formation of $\text{Cr}_2\text{O}_3(\text{s})$ by the electrochemical reduction of high valent chromium oxide and oxyhydroxide species, in particular $\text{CrO}_3(\text{g})$ and $\text{CrO}_2(\text{OH})(\text{g})$, is most important for the observed degradation of the electrochemical properties of the cell since $\text{Cr}_2\text{O}_3(\text{s})$ is formed at those sites which are particularly well suited for the cathodic oxygen reduction. The formation of $\text{Cr}_2\text{O}_3(\text{s})$ can thus inhibit the oxygen reduction necessary for the operation of an SOFC and may lead to polarization losses.

Furthermore, the formation of $\text{Cr}_2\text{O}_3(\text{s})$ can be coupled to other chemical reaction with perovskites $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$, as well as with both perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ and YSZ. YSZ is treated as ZrO_2



The driving force for the reaction (18) is essentially the formation of the $(\text{Cr}_{1-y}\text{Mn}_y)\text{O}_{1.5-\delta}$ oxide solution or spinel. Reaction (19) occurs only if the negative Gibbs energy exceeds the Gibbs energy change of SrZrO_3 formation and its subsequent dissolution in a perovskite compatible with ZrO_2 . The dissolution of the chromia and precipitation of the spinel phase may deteriorate the electrochemical properties of the perovskite.

A reduction of the evaporation rate of volatile chromium oxides and hydroxides can be achieved by using a steel that forms an oxide layer on top of the chromia scale. Fe–Cr model alloys with variations in chromium content and additions of Ti and/or Mn as well as additions of La, Ce, Zr and Y were studied for potential application in interconnect [19]. Fig. 9 shows the electrical resistances of the oxide scales during exposure up to 500 h in air at 800 °C. These results are compared with those for a typical ceramic $(\text{La,Sr})\text{CrO}_3$ interconnect of 5 mm thickness and chromia-forming alloys Fe25CrLa and Fe25CrZr. After reaching stable conditions, all tested alloys showed lower electrical resistances than the ceramic interconnect. The alloys containing Ti and La exhibited relatively low electrical resistance. The $(\text{Mn,Cr})_3\text{O}_4$ spinel-forming steels showed lower chromium evaporation rates than pure chromia-forming alloys.

4. Benefit of SOFC operation at higher cell voltage

SOFC systems are presently rated at a cell voltage of 0.7 V/cell. While this is a reasonable approach for performance comparisons and exhibits a high electric power output (>50% of the maximum), there are also some disadvantages. As seen in Fig. 10, the cell efficiency is restricted to 56% by the electricity/heat ratio of 1.3. The cell generates approximately 0.75 W heat/W electricity. Removal of the heat needs large amounts of air which affect stack, heat exchanger and blower design.

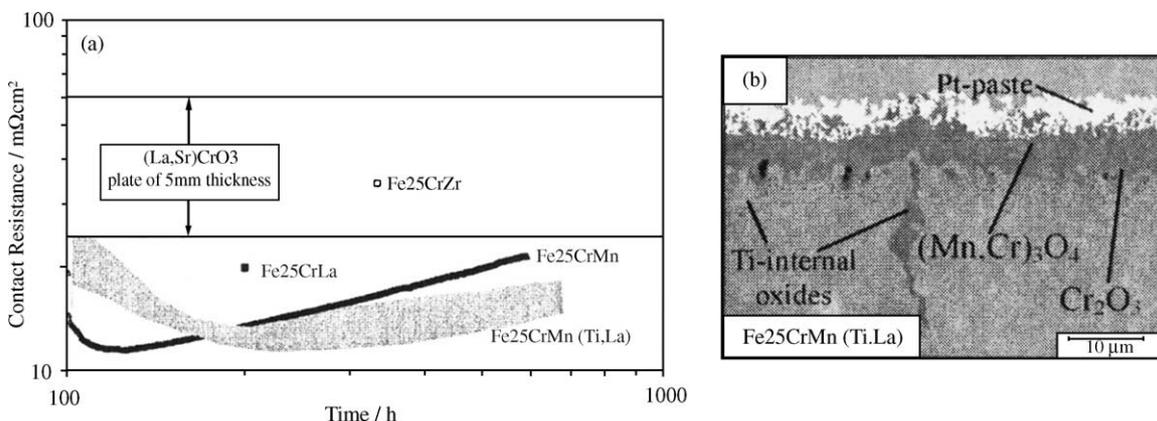


Fig. 9. (a) Electrical contact resistance of selected model alloys at 800 °C in air compared with ceramic interconnect of 5 mm thickness. (b) Microstructure of the scale formed on model alloy Fe25CrMn (Ti,La) after 600 h conductivity testing in air [19] (reproduced by permission of The Electrochemical Society).

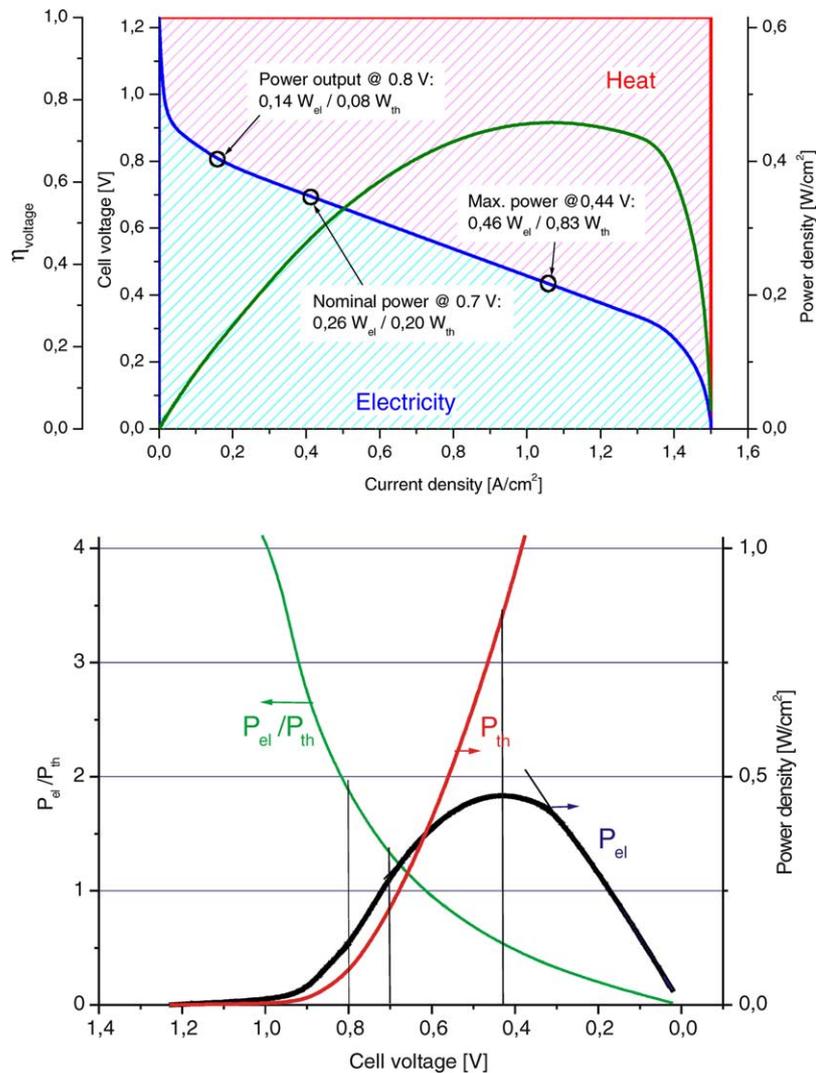


Fig. 10. Comparison of specific electricity and heat generation in an SOFC.

A rise of the cell voltage for example to 0.8 V/cell implies an 80% increase in cell area and therefore stack size for the same electric output. However, the electricity/heat ratio increases from 1.3 at 0.7 V to 1.75 at 0.8 V. The cell efficiency is then raised to 64%. The resulting lower heat load reduces the size of peripherals like tubing, heat exchanger and blower, and also the power consumption of active cooling systems like blowers and pumps.

5. Conclusions

Solid-oxide fuel cells have the potential market competitiveness. Significant advances are being made in SOFCs including realization of SOFC operating at temperature <800 °C and direct supply of hydrocarbon fuels. The aging of the cell components contributes significantly to the decrease of long-term performance of SOFCs under steady state operation. Aging mechanisms in compo-

nents strongly depend on the materials, microstructures and operating conditions. Development of new materials, optimization of microstructures and lowering of operating temperatures are desirable for the long-term stability of SOFC and the possibility for direct fuel supply. Cell voltage is an important parameter in SOFC system design. It is beneficial to operate the cell at higher voltage.

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