

# Chapter 2

## Overview of Intermediate-Temperature Solid Oxide Fuel Cells

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### 2.1 Introduction

The first breakthrough in solid oxide fuel cell (SOFC) technology was achieved by Westinghouse Power Corporation (WHPC; currently Siemens Power Generation Corporation) [1] in the late 1980s in their efforts in establishing tubular SOFCs with the following technologically important points:

1. Optimizing the materials [yttrium-stabilized zirconia (YSZ) for the electrolyte, lanthanum strontium manganite for the cathode, nickel for the anode, and lanthanum magnesium chromite for the interconnect].
2. Adopting an excellent processing technology of electrochemical vapor deposition (EVD) [2] that has extraordinary advantages in fabricating dense films on porous materials or in anchoring nickel on YSZ.
3. Adopting a sealless tubular stack design to avoid usage of sealant materials.
4. Aiming for stationary applications.

This breakthrough leveraged up the development of the SOFC stacks/systems from the R&D stage to a more realistic stage with specifically targeted market sectors. The long operation life was successfully demonstrated, and also the high conversion efficiency from natural gas to electricity was demonstrated as 47% Lower Heating Value (LHV) for stationary 100-kW SOFC systems and as 52% for combined SOFC-gas turbine systems.

Immediately after the first breakthrough with sealless tubular cells, detailed analyses were made by Ackerman at the Argonne National Laboratory (ANL) to identify the merits and demerits of the sealless tubular cells [3]. The main disadvantages were pointed out as follows:

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1. High fabrication costs because the EVD process utilizes metal chloride vapors in vacuum.
2. Low volumetric power densities because the electrical paths lie transversely along the cathode layer in tubular cells.

Since then, various attempts [4–6] have been made to investigate the following main points:

1. Planar cells to improve the power density.
2. Tubular cells to lower the fabrication cost or to increase the power density.

The next new wave in developing solid oxide fuel cells arose around the mid-1990s. One of the biggest achievements in this period was the discovery of a new oxide ion conductor, namely, lanthanum strontium gallium magnesium oxides (LSGM), by Ishihara in 1994 [7, 8]. Another important impact on SOFC technology was the proposal of using SOFCs as auxiliary power units for automotive applications by BMW and Delphi [9]. A similar proposal was made by ANL for monolithic SOFCs in the late 1980s [10] in their efforts to overcome the demerits of sealless tubular cells. Even so, the proposal by BMW/Delphi was based on the important trends in recent SOFC technology development; that is, lowering the operational temperature for using metal interconnects. In view of this, the discovery of a new electrolyte has further facilitated this trend.

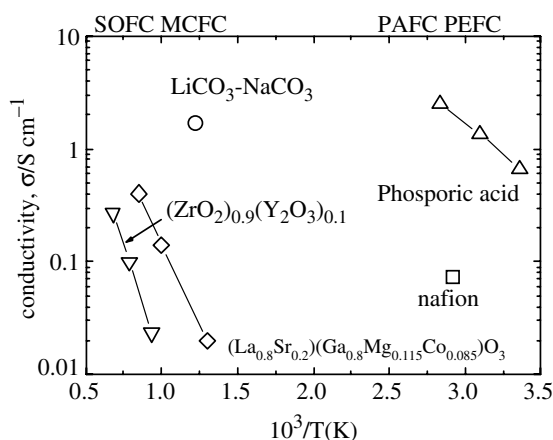
Quite recently, a small SOFC system for residential application has been constructed by Kyocera and tested by Osaka Gas [11]. These test results indicate surprisingly high stack efficiencies, more than 50% Higher Heating Value (HHV) during the steady-state operation and 42%–48% LHV as the averaged system net efficiency over a 24-h service period in a residential house. Similarly, Mitsubishi Materials Corporation and The Kansai Electric Power Co., Inc. also achieved high conversion efficiencies by using a Co-doped LSGM (LSGMC) electrolyte. These achievements indicate that the development stage of the SOFC technology is apparently being stepped up and that a new era of SOFC developments has already started. The important key word for this new era is the “intermediate-temperature SOFCs.” In this chapter, these recent developments associated with the intermediate-temperature SOFCs are reviewed with an emphasis on the stack/system development.

## **2.2 Characteristic Features of Solid Oxide Fuel Cells**

### ***2.2.1 Merits and Demerits of SOFCs***

Solid oxide fuel cells make use of the high-temperature oxides as electrolyte. Figure 2.1 compares the conductivities of common electrolytes that are utilized in various fuel cells; namely, phosphoric acid fuel cells (PAFC), polymer electrolyte fuel cells (PEFC), molten carbonate fuel cells (MCFC), and solid

**Fig. 2.1** The conductivity of typical electrolytes for fuel cells: PAFC, PEFC, MCFC, and SOFC [12]



oxide fuel cells (SOFC) [12]. When compared with liquid electrolytes such as molten alkali carbonates or phosphoric acid, the conductivity of solid electrolytes is not high; this implies that the solid electrolyte should be fabricated into a thin film with an appropriate technique. Another important feature appearing in Fig. 2.1 is that the activation energy of conductivity is quite large for solid oxide electrolytes; thus, the lower limit of operating temperature range for oxide electrolytes is dictated by the Joule loss. This limitation inevitably leads to a high-temperature operation for solid oxide fuel cells.

However, this condition provides some merits for solid oxide fuel cells. The most important one is that the operation temperature can be higher than the reforming temperature so that the heat required for the reforming process may be supplied from the SOFC exhaust heat, and this is one of the reasons why the efficiency of SOFCs can be high. For a similar reason, SOFCs are appropriate for hybrid systems with gas turbines in which further increase in efficiency can be expected by postcombustion of remaining fuels.

The demerits of high-temperature operation appear as higher thermal stresses and longer start-up times. Cells are made up of all solid components so that thermal stresses may result from thermal expansion coefficient mismatch among cell components or due to volume changes during redox cycles or chemical reactions. When the operation temperature is high, large temperature differences tend to develop, causing more severe conditions for thermal stresses. In addition, higher operating temperatures inevitably require longer start-up times.

All solid fuel cells have the important merit of long life expectation. In other words, fuel cells with liquid electrolytes suffer from degradation due to severe corrosion. In solid oxide fuel cells, the lifetime is not determined by such a degradation mechanism. On the other hand, however, another demerit may arise from the fact that solid oxide fuel cells are made up of all solids, implying difficulty in constructing SOFC stacks [4]. To ensure the gas tightness of SOFC stacks, it is essential to fabricate stacks by high-temperature sintering processes

or by physically activated processes such as the EVD process. The latter is convenient for fabricating dense films on a porous substrate but expensive for competition with inexpensive gas engines. The former is economical but needs high-temperature exposure of materials, leading to deterioration of materials due to interdiffusion across interfaces. Even when stacks are well fabricated as gas-tight stacks, thermal stresses caused by temperature variations lead to mechanical weakness. The merits and demerits of SOFCs are shown briefly in Table 2.1.

**Table 2.1** Merits and demerits of solid oxide fuel cells

	Merits	Demerits	Solutions
High-temperature operation	High conversion efficiency Hybrid system with gas turbines Cogeneration system	Thermal stress Starting up time	Sealless tubular
All solid	Long life No need for electrolyte management or water management	Difficulty in stacking cells Volume changes cause degradation	Monolithic cells Anode support cells Micro tubes
Electrochemical cells	Little $\text{NO}_x/\text{SO}_x$ emission No use of precious metals	Needs for fuel treatment Little scale merits High fabrication cost	1 MW class Several times 10 kW Several kilowatts (kW)
Membrane reactor	$\text{CO}_2$ removal	Difficulty of 100% fuel utilization	Hybrid system with gas turbine (GT)

These features of SOFCs affect selection of appropriate materials that must meet a number of physicochemical requirements. An additional but important requirement is materials compatibility to achieve chemical and mechanical stability. For example, even when excellent performances are measured for electrode materials, they cannot be used if their compatibility with the electrolyte is not good. A typical example is  $\text{LaCoO}_3$ , which exhibits excellent electrochemical activity; however, the reactivity of this material with YSZ is significant and the thermal expansion mismatch with YSZ is large. In view of this, the selection of the electrolyte material mainly dictates the additional requirements for other materials.

### 2.2.2 Issues for Intermediate-Temperature SOFCs

The first breakthrough in solid oxide fuel cells by WHPC was made by using yttria-stabilized zirconia (YSZ) so that the operation temperature could be around  $900^\circ\text{--}1000^\circ\text{C}$ .

Technological motivation for lowering the operation temperature can be summarized as follows:

1. In the beginning, strong interest arose in utilization of metal interconnects instead of  $\text{LaCrO}_3$ -based oxide interconnects [13]. Because of the severe corrosion of metals at high temperatures, operation temperature needs to be lowered.
2. Thermodynamic conversion efficiency increases with decreasing temperature for reformed gas (a mixture of CO and hydrogen).
3. Sealing technique becomes less difficult with lowered temperature.
4. For a small system, radiation heat loss becomes less severe by decreasing temperature. Hence, heat management becomes easier at lower temperatures [11].

On the other hand, decreasing operation temperature gives rise to additional materials issues as follows:

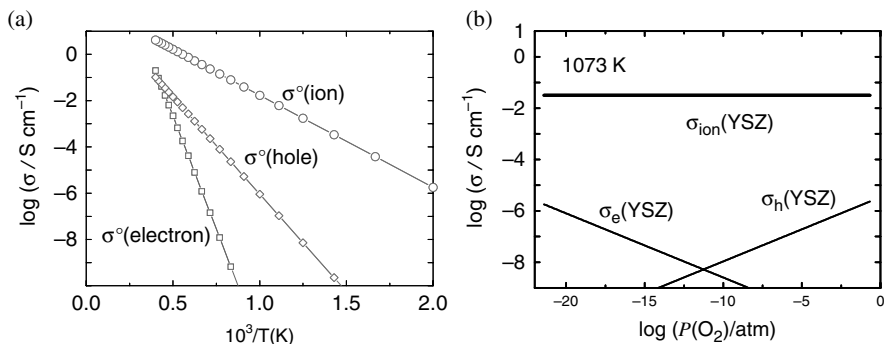
1. The oxide ionic conductivity decreases rapidly with decreasing temperature. As indicated in Fig. 2.1, the activation energy for the ionic conductivity is high so that the ionic conductivity drop is rather significant. To establish intermediate-temperature SOFCs, it is essential to have faster oxide ion conductors or to have a good method of fabricating a thinner electrolyte film. In view of these concerns, anode-supported cells are one of the possible technological solutions.
2. Usually, the electrode activity also decreases drastically with decreasing temperature, which makes it necessary to utilize more active electrode materials.
3. For the anode, nickel is still the best choice for operation in the intermediate-temperature region. Most frequently observed effects on nickel anodes are sulfur poisoning. It is well known that degradation caused by hydrogen sulfide becomes more severe with decreasing temperature.
4. For the cathode, Cr poisoning is severe on the lanthanum strontium manganites and becomes worse with decreasing temperature, against expectations.

In what follows, the materials aspects of intermediate-temperature SOFCs are described.

### 2.2.2.1 Electrolytes and Conversion Efficiency

The conduction properties of electrolytes are the most important factors in determining the operational temperature [11]. Here, the conversion efficiency is described in terms of conduction properties. The oxide ion conductivity determines the area-specific resistance contributed by the electrolyte. The contribution increases with increasing thickness of the electrolyte plate (film).

The oxide ion conductivity exhibits an Arrhenius-type behavior (Fig. 2.2). For YSZ, no oxygen potential dependence is observed over a wide oxygen partial pressure range applicable to solid oxide fuel cells. For electron and hole conductivities, the oxygen potential dependence is given by the following equation:



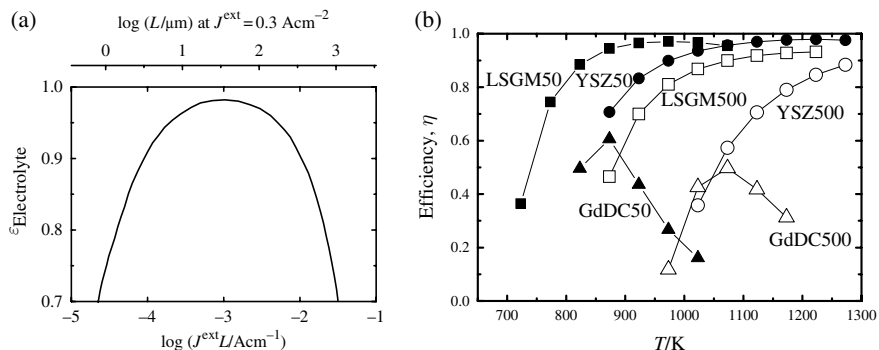
**Fig. 2.2** Characteristic features of conductivities of YSZ as functions of (a) temperature and (b) Oxygen potential [14]

$$\sigma(\text{el}) = \sigma^{\circ}_{\text{electron}} p(\text{O}_2)^{-1/4} + \sigma^{\circ}_{\text{hole}} p(\text{O}_2)^{1/4} \quad (2.1)$$

Here,  $\sigma^{\circ}_{\text{electron}}$  and  $\sigma^{\circ}_{\text{hole}}$  are the normalized contribution of electrons and holes at 1 atm oxygen partial pressure. Their temperature dependencies are compared in Fig. 2.2(a) together with the oxide ion conductivity. Since the activation energies for electron and hole conduction are larger than that of the oxide ion conduction, the contribution of electron conduction becomes large when temperature increases. At 1073 K, as illustrated in Fig. 2.2(b), the oxide ion conductivity is several orders of magnitude higher than those of electrons and holes, indicating that YSZ is an excellent electrolyte for fuel cells. At temperatures as high as 2000 K, however, YSZ may no longer be utilized as an electrolyte but can be characterized as a mixed conductor.

The electrical properties determine the energy conversion losses that occur inside the electrolyte plate. The conversion losses can be expressed as a deviation from the theoretical conversion based on the Gibbs energy. In Fig. 2.3(a), the conversion losses are plotted as a function of products of current density ( $J^{\text{ex}}$ ) and electrolyte thickness ( $L$ ). For large values of  $J^{\text{ex}}L$ , the conversion efficiency,  $1-\eta$  (electrolyte), decreases with increasing  $J^{\text{ex}}L$ ; this is known as the Joule effect. On the other hand, even for small values of  $J^{\text{ex}}L$ ,  $1-\eta$  (electrolyte) decreases with decreasing  $J^{\text{ex}}L$ ; this is called the shorting effect caused by electronic conduction. With this, oxide ions are transported and take part in electrochemical reactions without generating electricity, which can be regarded as an ordinary chemical reaction of fuel with permeated oxygen gas (oxide ion and holes). In view of this, the shorting effect can also be called the oxygen permeation effect. By combining the Joule effect and the shorting effect, the deviation from the Gibbs energy conversion efficiency can be characterized by a curve with a maximum point.

A similar maximum behavior is observed even for the temperature dependence when the thickness of electrolyte and the current density are fixed as shown in Fig. 2.3(b). In this figure, three different electrolyte materials are

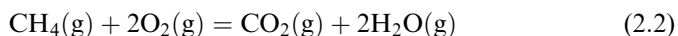


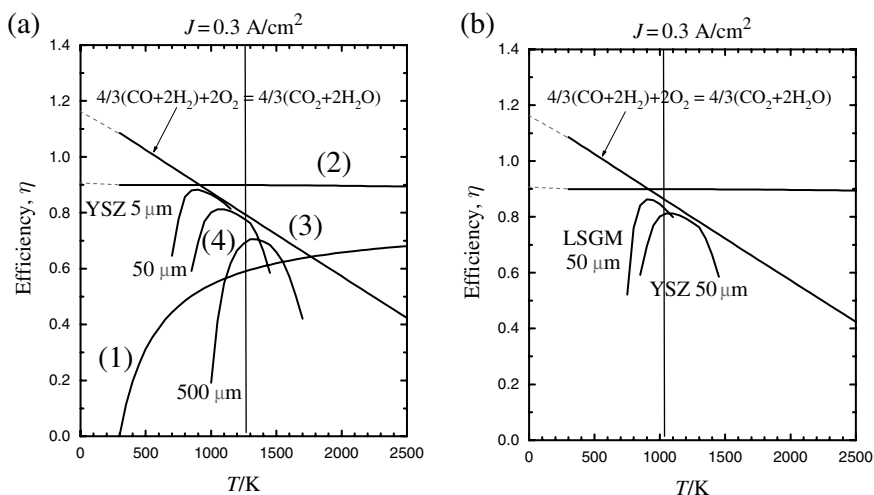
**Fig. 2.3** Gibbs energy-based conversion loss occurring in electrolytes due to Joule effects and shorting effects: (a) as a function of products of current density and thickness at a given temperature (1273 K) [14] and (b) as a function of temperature for a given current density ( $0.3 \text{ A/cm}^2$ ) with parameter of thickness ( $\mu\text{m}$ ) [12, 14]

compared with each other. As shown in Fig. 2.2(b), the electronic contributions in YSZ are small so that the efficiency lowering is very small over a wide temperature range. For  $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.8}\text{Mg}_{0.2})\text{O}_{2.8}$  (LSGM), the region of high efficiency extends to a lower temperature than for YSZ, because the oxide ionic conductivity of LSGM is higher so that the Joule effect is smaller. For Gd-doped ceria (GDC), the efficiency at high temperatures is quite low due to the large contribution of the electronic conduction.

The energy conversion efficiency is usually discussed in terms of the enthalpy-based conversion rate. For example, theoretical efficiency is defined as the ratio of the Gibbs energy change to the enthalpy change for fuel cell reaction. Therefore, the values just discussed should be transferred to the enthalpy-based ones. For this purpose, the thermodynamically theoretical conversion efficiency should be defined in a manner that enables comparison with other energy converters such as heat engines. Here, we start with methane as the common fuel. In Fig. 2.4(a), we compare several cases as a function of temperature:

1. Carnot efficiency is usually defined as  $w/q$ , where  $w$  is work to be done during one cycle, whereas  $q$  is high-temperature heat to be used. In the present case, we start with methane chemical energy (enthalpy), which has a higher quality than high-temperature heat. To create high-temperature heat from the chemical energy of methane, we lose some part of it during the combustion process. Line (1) in Fig. 2.4(a) shows the Carnot efficiency after subtracting this effect.
2. Line (2) is the ratio of Gibbs energy to enthalpy for the complete direct oxidation of methane:





**Fig. 2.4** Comparison in conversion efficiency: (a) (1) Carnot efficiency after correction of self-heating of methane combustion, (2) methane direct oxidation, (3) oxidation of reformed gas, (4) oxidation of reformed gas after correction for conductive properties of YSZ in given thickness; (b) comparison between YSZ and LSGM in the same thickness of 50  $\mu\text{m}$

Because these two quantities,  $\Delta H$  and  $\Delta G$ , have no temperature dependence, the derived efficiency is high and independent of temperature. In actual fuel cells, this reaction could not proceed, because nickel anodes are not active to the direct oxidation of methane.

3. Line (3) is for electrochemical oxidation of hydrogen and CO after reformation process. Methane reforming can be achieved by using water vapor or anode-circulated gases. Here, we assume that the anode gas is circulated, simply because we would like to utilize the methane alone as a starting material for comparison purposes. The anode gas circulation makes it easy to compare the case with Carnot cycles in which external water is not used. Assumption is also made for the point that the heat required for the reforming process is supplied from the heat emitted from the fuel cells. This is the essentially different point from the reforming process connected to the PEFC system, in which additional fuel should be burned to supply the required heat. This benefit of utilizing internal heat appears as the feature that the Gibbs energy conversion rate for the reformed gas shifts to quite high values in the vicinity of the reforming temperatures around 900 K in Fig. 2.4(a). Even so, the Gibbs energy-based conversion rate decreases with increasing temperature above the reforming temperature; this implies that the solid oxide fuel cells to be operated around the reforming temperature are expected to have the highest conversion efficiencies.
4. Lines (4) are combined effects of the Gibbs energy-based rate [line (3)] and the lowering effects resulting from the electrolyte conductivity properties



from the Gibbs energy-based rate. For YSZ electrolyte, three values corresponding to different thickness values are taken from those in Fig. 2.3(b). Figure 2.4(a) shows, in a clearer manner, the effect of electrolyte thickness. For YSZ, the thickness of 50  $\mu\text{m}$  adopted first by WHPC in the EVD process provides rather good efficiency even at a temperature lower than 1273 K. The thinner YSZ can provide more efficient SOFC systems. In view of this, the anode-supported cells are of strong interest and importance for developing the intermediate-temperature SOFCs.

In Fig. 2.4(b), comparison is made between YSZ and LSGM for identical thickness values of 50  $\mu\text{m}$ , which indicates the superiority of higher oxide ion conductors in the intermediate-temperature SOFCs. Particularly, technological conditions are quite different. For YSZ, anode-supported cells are inevitably required, whereas the self-supported cells can be operated around 1073 K for LSGM. Actually, Mitsubishi Materials Corporation successfully designed and manufactured SOFC systems based on the self-supporting LSGMC cells, confirming that the obtained efficiency is high, as is described in the following sections.

#### 2.2.2.2 Cathode

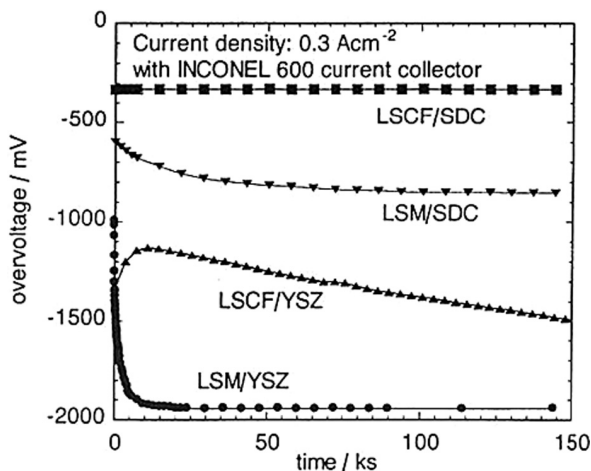
##### Relationship with YSZ and Cr Poisoning

In the first generation of SOFC to be operated around 1273 K, the lanthanum strontium manganites  $[(\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3]$ , LSM] have been well investigated because of their higher cathode activity and compatibility with the YSZ electrolyte [15]. Since the chemical stability was much more important in the first generation, LSM has been utilized widely in actual stacks. When LSM is used for intermediate-temperature SOFCs, it has been found that the performance of LSM on the anode support cells is degraded rapidly with decreasing temperature. In addition, LSM is poor against the Cr poisoning [16], which is caused by the chromium-containing vapors emitted from  $\text{Cr}_2\text{O}_3$  oxide scale on the metal interconnects.

Lanthanum strontium cobaltite  $[(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3]$ , LSC] was the first perovskite-type oxide investigated as a SOFC cathode in 1969 [17]. Even in this attempt, it was found that LSC degraded rapidly because of a chemical reaction with YSZ. Since then, major investigations on cathodes moved to the lanthanum strontium manganites. The recent trend of lowering operation temperature, however, leads again to the investigation of LSC,  $(\text{La}_{1-x}\text{Sr}_x)\text{FeO}_3$  (LSF), and  $(\text{La}_{1-x}\text{Sr}_x)(\text{Co}_{1-y}\text{Fe}_y)\text{O}_3$  (LSCF) by using the interlayer made up of doped ceria between YSZ and those perovskite cathodes.

It is interesting to see the work by Matsuzaki and Yasuda [18], who investigated Cr poisoning using different combinations of electrolyte and cathodes; as electrolyte, they selected YSZ and samarium-doped ceria (SDC), and LSM and LSCF were selected as cathodes. As shown in Fig. 2.5, a potential drop from Cr poisoning is largest and most rapid for LSM/YSZ, whereas LSCF/

**Fig. 2.5** Cr poisoning for different combinations of electrolyte and electrode, measured with a cathode half-cell in contact with a plate of INCONEL 600 by Matsuzaki and Yasuda [18]



SDC showed no decrease from Cr poisoning. These results indicate that the identification of electrochemical reaction mechanism is crucial in understanding Cr poisoning.

Table 2.2 summarizes and compares various features of perovskite cathodes from the aspect of valence stability. Valence stability is directly related with chemical stability and also indirectly with electrochemical activity through oxide ion conductivity.

**Table 2.2** Comparison among perovskite cathodes (LSM, LSF, LSC) in their trade-off relationship between chemical stability and performance with emphasis on the reaction with YSZ and Cr vapors [21]

Items	LSM	LSF	LSC
Valence stability	$\text{Mn}^{4+}$ stable	$\text{Fe}^{4+}$ unstable	$\text{Co}^{4+}/\text{Co}^{3+}$ unstable
$\text{O}^2$ conductive	Quite slow	Fast	Fast
Cathode mechanism	Three-phase boundary	Surfaces	
Reactivity with YSZ	Stable (A-site deficient)	$\text{SrZrO}_3$ formation	$\text{La}_2\text{Zr}_2\text{O}_7$ $\text{SrZrO}_3$ formation
Reactivity with Cr	$\text{Cr}^{3+}$ substitute	$\text{SrCrO}_4/\text{Cr}^{3+}$ substitute	$\text{SrCrO}_4/\text{Cr}^{3+}$ $\text{Cr}^{4+}$ substitute
Cr poisoning	Significant	Not seen in early stage, but degradation due to $\text{SrCrO}_4$	

The valence stability itself is defined as the thermodynamic properties, so that it is natural to expect that the chemical stability of perovskite oxides is related to the valence stability in addition to the stabilization energy of double oxides from the constituent oxides. Particularly, the reaction of perovskite oxides with YSZ has been well examined experimentally as well as thermodynamically.

The formation of  $\text{La}_2\text{Zr}_2\text{O}_7/\text{SrZrO}_3$  at the interfaces is accompanied with the reduction of transition metal oxides and precipitation of compounds with reduced valence ions [19]. Recently, chemical reactions of perovskite oxides with chromium-containing vapors have been analyzed in a similar manner, and it has been found that reactivity with chromium vapor is of the same order among the LSM, LSF, and LSC as reactions with YSZ [20, 21]. That is, the Sr component in the perovskite oxides can react with Cr vapors to form  $\text{SrCrO}_4$  for LSF and LSC but not for LSM, which exhibits the most severe Cr poisoning effect. This result implies that chemical reactivity alone cannot explain the Cr poisoning effect, because LSM exhibits most severe Cr poisoning effect, although LSM is most stable against reactions with Cr vapors.

The oxide ion vacancies in the perovskite  $\text{ABO}_3$  oxides are formed as a result of reduction of the B-site ions on substitution of  $\text{Sr}^{2+}$  ions to the  $\text{La}^{3+}$  (A) sites; this will lead to mixed conductivity of lanthanum strontium transition metal oxides. Even so, the oxide ion vacancy formation is competing with the oxidation of transition metal ions in the B sites. The latter depends on the valence stability of the transition metal ions. For the case of  $(\text{La},\text{Sr})\text{MnO}_3$ , the tetra valence of manganese ions is stable in the perovskite lattice so that the Sr substitution gives rise to the oxidation of manganese ions from  $3+$  to  $4+$  and to essentially no oxide ion vacancy formation. As a result, the oxide ion conductivity in LSM is not high. This fact affects the reaction mechanism; that is, only the three-phase boundaries (TPB) are electrochemical active sites for the LSM cathode, whereas the high oxide ion conductivity in LSF and LSC provides wider distribution of electrochemically active sites. This difference on the distribution of active sites in relationship to the oxide ion conductivity leads to different features in the oxygen flow and associated with the oxygen potential distribution.

This difference in the oxygen flow and distributions of active sites and of oxygen potential provides a good basis of explaining the difference in the Cr poisoning. For LSM, the oxygen flow has to be concentrated in the TPB where Cr tends to be deposited, whereas the chemical reaction with Cr vapors can take place at any point of the LSF or LSC surfaces, but the oxygen flow can be changed to avoid such reaction sites. For long-term stability, however,  $\text{SrCrO}_4$  formation should be avoided to maintain mechanical stability as well as chemical stability.

It is generally considered that the cathodes for intermediate-temperature SOFCs should be electrochemically more active than those cathodes in the first generation, namely, LSM. When LSF, LSC, or LSCF is used as cathode, an interlayer made of doped ceria becomes inevitable to avoid chemical reactions between cathode and YSZ. In addition, such cathodes should be also protected against Cr vapors. This approach gives rise to a complicated layer structure across the electrolyte to current collector and makes it difficult to fabricate such complicated layers. For example, the following points are important:

1. Doped ceria–YSZ interface. Solid solutions between doped ceria and YSZ provide interesting systems for investigating the transport and related properties [22, 23]. That is, the ionic conductivity has a minimum in the middle of the Ce concentration range, whereas the electronic conductivity has a maximum. Similarly, the surface exchange reaction rate exhibit strong concentration dependence. This property suggests that when the doped ceria–YSZ interface was prepared in a well-bonded state at interfaces by sintering at high temperatures, interdiffusion takes place across the interface, forming a layer with high electrical resistance. Furthermore, interdiffusion sometimes gives rise to Kirkendall pores in the ceria side because of the differences in diffusivities of zirconia and ceria [24].
2. Strictly speaking, interfaces between perovskite cathode and doped ceria are not thermodynamically stable, and some chemical reactions can take place [21, 25]. In addition, cation diffusion can occur. In particular, Sr diffusion through doped ceria is important. There are some differences between LSF and LSC as far as reactivity and interdiffusion are concerned; that is, no products are formed for the diffusion couple between Gd-doped ceria (GDC) and LSC, because  $\text{GdCoO}_3$  exhibits no thermodynamic stability. In other interfaces, there arises a driving force of forming another perovskite phase from the dopant in ceria and the B-site ions (Fe or Co ions) in the perovskite; this is accompanied with Sr diffusion.
3. To obtain a stable interface between cathode and metal interconnect, it is essential to adopt a coating layer on the interconnect to prevent the migration of Cr from the metal alloys.

### Compatibility with LSGM

Immediately after the discovery of LSGM by Ishihara [7,8], it became clear that interdiffusion associated with LSGM is significant between LSGM and cathode electrode [26]; this makes it difficult to prepare cathode-supported cells in which the cathode–electrolyte interfaces are exposed to high temperatures. Currently,  $(\text{Sm,Sr})\text{CoO}_3$  is widely utilized as a cathode material on the basis of Ishihara's results [27].

Because  $(\text{Sm,Sr})\text{CoO}_3$  exhibits similar features to those of  $(\text{La,Sr})\text{CoO}_3$ , reactions with Cr vapors are also technologically important issues. That is, immediate degradation of SSC cathodes is not expected, but the formation of  $\text{SrCrO}_4$  leads to changes in microstructure and other properties. Particularly, the thermal expansion coefficients of the Sr-depleted cobaltites and of the formed  $\text{SrCrO}_4$  are both large.

#### 2.2.2.3 Anode

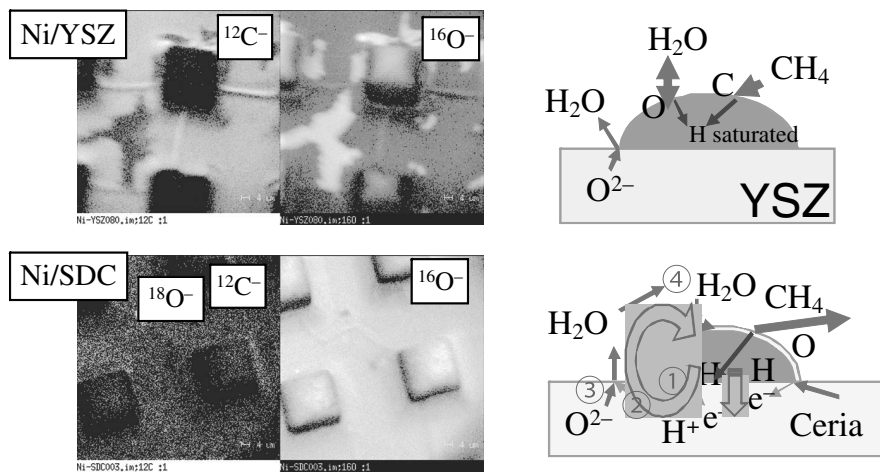
Even for the intermediate-temperature SOFCs, Ni is the best anode as far as the current technological status is concerned. Although a number of investigations have been made on oxide anodes, nickel cermet (*ceramic-metal*) anodes exhibit

excellent ability of dissociating hydrogen bonds. As the oxide component of cermet anodes, YSZ is frequently used. In recent years, ScSZ or doped ceria have attracted attention because characteristic features against carbon deposition or sulfur poisoning can be improved by the use of these oxides instead of YSZ.

### Nickel Anode

Technological issues associated with nickel anodes can be summarized as follows.

1. Sintering: In the first-generation SOFCs, sintering of nickel anodes and the associated degradation are one of the major issues because the high operation temperature promotes sintering during long operation times. Furthermore, nickel microstructure can be heavily damaged to form metastable Ni-C liquids in the presence of carbon. In the intermediate-temperature SOFCs, however, these mechanisms of sintering or change in microstructure caused by the Ni-C liquids are expected to diminish.
2. Carbon deposition: Nickel is weak against carbon deposition even in the intermediate-temperature region. There is an apparent effect of the oxide mixing on the carbon deposition behavior among various cermet anodes. Figure 2.6 depicts the different features of patterned Ni on YSZ or SDC without any electrochemical reactions under an atmosphere that is thermodynamically favorable to carbon deposition [28]. Surface species on nickel were detected by secondary ion mass spectrometry (SIMS), indicating that these are



**Fig. 2.6** SIMS analysis for detection of dissolved species on surfaces of nickel on different substrates under identical gaseous atmospheres that facilitate carbon deposition. The difference between YSZ and SDC can be explained by using a mass transfer model including the dissolution of water into SDC together with enhanced surface exchange reaction rates [28]

not adsorbed species but dissolved atoms. For Ni/YSZ, carbon covers almost the entire surface of nickel and only a small amount of oxygen is present on the surface. Under the same condition, Ni/SDC exhibits quite different features of nickel surface. That is, the nickel surface is covered by oxygen instead of carbon. This observation can be reasonably explained by considering the mass transfer mechanism in which nonnegligible water solubility in ceria, and enhanced surface reaction at the ceria surface, can be accounted for as different features. Under a polarization of the Ni/YSZ combination, a similar coverage of oxygen was observed on nickel, indicating that the above mechanism is closely related with the anode reaction mechanism.

3. Sulfur poisoning: From the earlier stages of the development of SOFCs, it has been well known that, in the presence of a small amount of hydrogen sulfide, the anode activity is lowered but will recover after switching back to non-hydrogen sulfide fuels [29]. In addition to this reversible lowering activity, nickel anodes show irreversible degradation at higher concentration of  $\text{H}_2\text{S}$  or at lower temperatures.
4. Redox cycle tolerance [30]: As anode-supported cells have been investigated extensively, redox cycles are recognized as quite important. One reason is that the anode-supported cells inevitably have a sealing problem on their edges. Because the anode is used as the supporting body, its mechanical stability becomes crucial. Another reason originates from the purge gas. When nitrogen is used as a purge gas, nickel anodes are always protected against reoxidation. However, for cases where nitrogen cannot be used due to system requirements, etc., stability during redox cycles becomes also a crucial technological matter. This phenomenon is closely related with diffusion of Ni and reconstruction of microstructure on reduction from NiO to Ni; this is because diffusion of Ni in the metal phase is faster than  $\text{Ni}^{2+}$  ions in the oxide. On the reduction of NiO in a mixture of NiO and YSZ (or other oxides), fine powers of nickel are formed, and then the electrical path will be established using powders by diffusion in the framework of YSZ. On reoxidation of nickel, NiO does not move so that volume expansion on oxidation takes place in the framework of YSZ. Because nickel was moved from the original position, the reoxidation gives rise to partial destruction of the framework as a result of a single redox cycle.

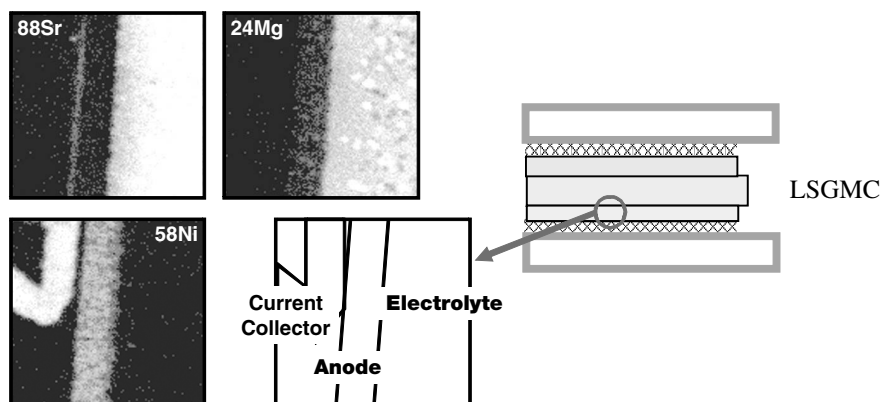
These features are closely related with the selection of the oxide component in cermet anodes. When  $\text{Sc}_2\text{O}_3$ -stabilized zirconia (ScSZ) is used instead of YSZ, some improvements have been obtained for carbon deposition [31] or resistance for sulfur poisoning [32]. These degradations should be discussed on the basis of the anode reaction mechanism. Even so, a large number of investigations have been made on reaction mechanisms, but unfortunately no reasonable agreement has been obtained among researchers. Here, a brief discussion is made about the role of the oxide component.

The surface reaction rate and the water solubility in ScSZ are found to be about the same as those of YSZ [33]; this implies that merits of using ScSZ may originate from properties such as the oxide ion conductivity or the cation

diffusivity affecting the microstructure of cermet anodes. In particular, higher oxide ion conductivity values positively affect the anode activities against carbon deposition or sulfur poisoning. As to carbon deposition, the water vapor emitted from active sites may have strong effects of avoiding carbon deposition by transferring oxygen atoms from the electrolyte to the nickel surface. When the current density is the same, the same amount of water vapor should be emitted. So, effects of higher oxide ion conductivity appear only in the distribution of electrochemically active sites. When the oxide ion conductivity is low, only the TPB located at the bottom of the anode layer becomes active, whereas the TPB even far from the bottom can be active when the oxide ion conductivity is high in the oxide component of cermet anodes. For the case of sulfur poisoning, the equilibrium shift should be considered as a function of anode overpotential as well as fuel utilization. Here, the overpotential should be related to the oxide ion conductivity.

### Nickel Anode with LSGM Electrolyte

For the LSGM electrolyte, the doped ceria is used as the oxide component in cermet anodes. The interface between doped ceria and LSGM is rather stable, although some interdiffusion occurs. One of the biggest issues associated with the nickel anode used together with LSGM electrolyte is that the dissolution of NiO into perovskite phase takes place significantly during the high-temperature sintering process of cells; this occurs because in air the  $\text{LaNiO}_3$  perovskite phase is rather stable so that NiO can be easily dissolved into the LSGM/LSGMC phases. In a worst case, NiO can penetrate completely to the cathode side. This phenomenon should be avoided, because NiO in LSGM can be reduced again to Ni metal by hydrogen so that the reduced Ni can cause electronic shorting paths inside the LSGM electrolyte. Figure 2.7 shows the distribution of



**Fig. 2.7** The elemental distribution detected with SIMS technique after 24-h operation of sealless disk-type cells made by Mitsubishi Materials Corp. [34]

elements in an actual LSGMC-based cell operated for 24 h obtained by secondary ion mass spectroscopy (SIMS) technique. The cell was fabricated and tested by Mitsubishi Materials Corporation [34]. It is clearly seen that the Ni dissolution into the LSGMC layer was successfully prevented during the fabrication process.

### Oxide Anodes

Recently efforts have been made on oxide anodes. The main reason for such investigations is to overcome the demerits of Ni cermet anodes as just described. Although the oxide anodes should be in service under a reducing atmosphere, the fabrication is usually performed in air so that oxide anodes should be stable at both oxidative and reductive atmospheres. This requirement is similar to those for oxide interconnects, implicitly indicating that material selection becomes severe to meet the chemical stability requirement.

Doped ceria and doped lanthanum chromites were investigated a long time ago because ceria is a mixed conductor in a reducing atmosphere, whereas lanthanum chromites are typical candidates for oxide interconnects. Neither of the materials shows good performance as an anode. In recent years, other types of perovskite oxides have attracted attention, as is described in other chapters of this book. The basic trade-off relationship associated with oxide anodes is stability versus performance.

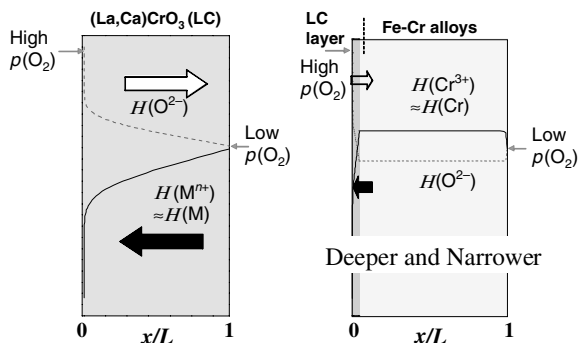
#### 2.2.2.4 Metal Interconnects

The reasons to utilize metal interconnects [13] instead of oxide interconnects [35, 36] may be listed as follows:

1. Material cost: La in the oxide interconnect is expensive, whereas ferritic alloys can be regarded as inexpensive.
2. Difficulty in fabricating  $\text{LaCrO}_3$ -based interconnects: Particularly, sintering in air is the most challenging. Although no SOFC stacks can be fabricated without establishing an appropriate technology for fabricating dense oxide interconnects, only a few manufacturers have succeeded in sintering oxide interconnects properly and constructing them into SOFC stacks. On the other hand, fabrication of metals is usually much easier than that of the  $\text{LaCrO}_3$ -based oxides. For oxide dispersed alloys such as  $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ , however, special technology is required to fabricate these into a shape for SOFC stacks.
3. High thermal conductivity: Management of temperature distribution inside stacks is essential in solid oxide fuel cells to protect the fragile ceramic components.
4. High mechanical stability: To moderate the thermal stresses in ceramic systems, it is essential to shorten the relaxation times for thermal fluctuations by using materials with low thermal expansion coefficients and high thermal



**Fig. 2.8** Oxygen potential distributions in the oxide interconnects and the metal interconnects. Inside the oxide, the oxygen potential distribution is determined by the oxide ion and electron conductivity, whereas the surface oxide scale determines the main features of the metal interconnects



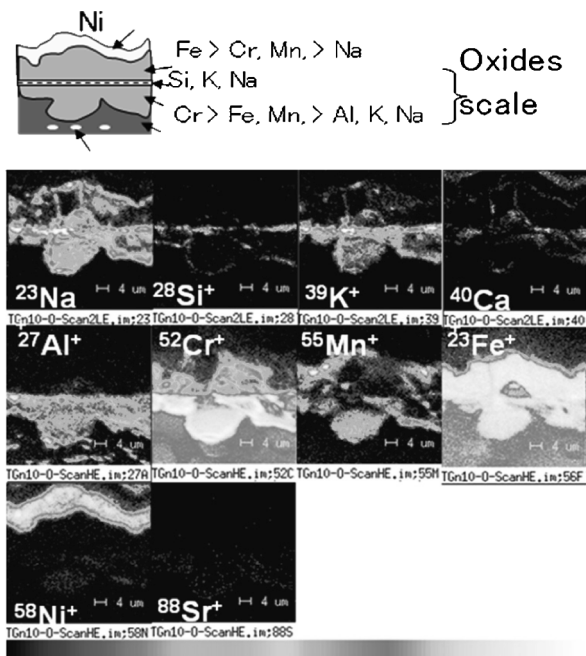
conductivities. Because YSZ electrolyte cannot meet such requirements by itself, it becomes essential to use metal components in SOFC stacks.

From the physicochemical point of view, the aforementioned interconnects can be compared in terms of their oxygen potential distribution (Fig. 2.8). In the  $\text{LaCrO}_3$ -based interconnect, a steep oxygen potential gradient appears in a thin layer on the air side, mainly because of extremely small oxide ion vacancy concentration and, hence, low oxide ion conductivity in the oxidative side. In the metal interconnect, the major steep oxygen potential drops appear in the oxide scale region in both fuel and air sides, and correspondingly the oxygen potential values inside metals are maintained at quite a low level. This finding implies that in the metal interconnect, the control of the mass transfer in the oxide scale vicinity is essential in judging the appropriateness of the materials.

Technological issues associated with metal interconnects can be summarized as follows:

1. Thermal expansion coefficients: For high-temperature utilization, Ni-Cr-based alloys are excellent from the anticorrosion point of view. Even so, such Ni-Cr alloys have high thermal expansion coefficients dictating a larger match with YSZ. Cr-based alloys developed by Siemens/Plansee have an essentially similar thermal expansion coefficient as YSZ. This alloy was utilized by Sulzer Hexis. Alternatively, Fe-Cr ferritic alloys are frequently utilized. Although complete matching in thermal expansion coefficient with YSZ is not obtained, Ni-Cr alloys provide considerable improvement.
2. Stable oxide scale: Corrosion affects SOFC stacks in two distinct ways. First, it increases the electrical resistivity. In normal configuration of cells, the electrical path usually penetrates across the oxide scale, which implies that growth of oxide scale makes a contribution to increase the area-specific resistivity. Another aspect of oxidation is related to mechanical stability. Growth of an oxide scale is inevitably accompanied with a volume change,

**Fig. 2.9** Anomalous oxidation of metal interconnects. The Na component migrated from the glass sealing materials was detected in anomalously corroded regions. The iron component in alloys moved out from the corroded area to anomalously expanded regions [37]



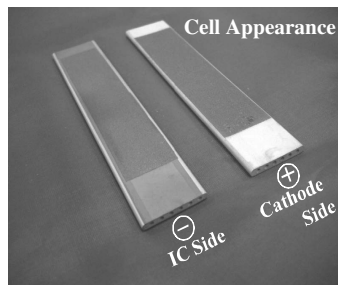
causing mechanical instability. From these, the oxide scale of a metal interconnect should be thin and electrically conductive.

3. Anomalous oxidation: In some cases, oxide scale made up of  $\text{Cr}_2\text{O}_3$  gets broken and can no longer serve as a protective layer; as a result, the iron component in alloys may become anomalously oxidized away from the scale. Typical features of such a phenomenon is shown in Fig. 2.9, in which anomalous oxidation of ferritic alloys in the presence of glass sealing materials is analyzed by using the SIMS technique detecting several times 10 ppm of the Na component [37]. In this particular experiment, the Na component is thought to have migrated from the glass sealing materials. Even so, Na contamination can commonly take place. It is a phenomenon similar to hot corrosion caused mainly by NaCl and/or  $\text{Na}_2\text{SO}_4$ .
4. Chromium poisoning: In the air side of the interconnect, Cr volatilization becomes an issue, because the perovskite cathodes tend to exhibit the Cr poisoning effect. In particular, the manganite cathodes show severe Cr poisoning. To avoid this, several attempts have been made on the metal interconnect side. Cr volatilization depends on the  $\text{Cr}_2\text{O}_3$  activity of the oxide scale. One way is to form a spinel phase on the inner  $\text{Cr}_2\text{O}_3$  scale. In typical ferritic alloys,  $\text{MnCr}_2\text{O}_4$  is formed as the outer oxide scale. Cr poisoning does not cease even for such a case. To stop Cr volatilization completely, a spinel phase containing no chromium should be coated on the surface of metal interconnects.

### 2.2.3 Stack Design

The stack design and its fabrication process are quite important in developing the SOFC systems. For the case of the first-generation SOFCs, selection of materials was accompanied by adoption of the electrochemical vapor deposition technique and the sealless tubular design. For the intermediate-temperature SOFCs, utilization of metals is a key in selecting the fabrication technique and the design. Typical designs are as follows:

1. Sealless planar: Electrochemical cells made up of electrolyte, cathode, and anode are stacked with metal interconnects without using sealing materials. For example, disk-type planar sealless stacks have been constructed by Mitsubishi Materials Corporation. For this purpose, fuel and air are introduced through the central part of the respective cells. Outside the cells, the remaining fuel becomes combusted with air. Self-supporting cells are usually used for this design.
2. Planar cells with sealant: Fuel and air are separately controlled using sealing materials. Anode-supported cells are used for this design, which makes it necessary to seal properly the edge part of anode-supported cells.
3. Flattened tubes: Anode-supported or cathode-supported tubes are flattened so that there is no need to seal the side of the tubes. When both ends are open, at least the entrances are sealed. When one end is closed, there is a need for an additional pipe to introduce air or fuel. Normally, interconnect materials are fabricated simultaneously. For this purpose, oxide interconnects are more appropriate. Figure 2.10 shows the flattened tube cells fabricated by Kyocera to be operated at 750°C.
4. Micro tubes: Micro tubes without oxide interconnects are fabricated with cathodes and anodes. Current collection becomes a key issue in this design.
5. Metal-supported cell: Since metal-supported cells are still in the early stages of development, there is no defined stack design associated with metal-supported cells. There is a possibility of achieving gas tightness without using sealing materials.
6. Segmented in series: Fabrication process is complicated in this design. In addition, interconnects are also key materials. When the oxide interconnect



**Fig. 2.10** Flattened tube-type cells for a small SOFC cogeneration system by Kyocera (courtesy of Kyocera)

is adopted, the same ceramic processing can be applied. In other words, proper manufacturing techniques addressing the problems in air sintering are essential. When metal interconnects are used, it becomes crucial to find appropriate methods for simultaneous fabrication of metals and ceramics.

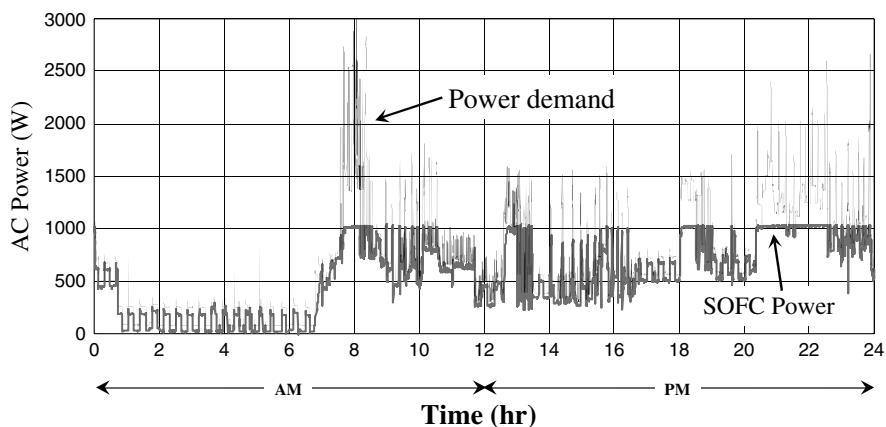
## 2.3 Development of Intermediate Temperature SOFC Stacks/Systems

### 2.3.1 *Kyocera/Osaka Gas*

After fundamental investigations on SOFC materials for a long period of time, Kyocera started the development of a small SOFC cogeneration system for residential houses in 2001. Although similar developments have been made by Sulzer Hexis for the last decade in cooperation with utility companies/local governments in Germany, there are some important differences between the two SOFC systems; that is, the Sulzer system is based on supplying 1 kW electricity and 2 kW heat for domestic utilization, whereas the Kyocera system has focused on those small systems with high conversion efficiency of generating electricity. This difference is mainly the result of strong requirements for electricity rather than heat in the Japanese market. To achieve this requirement technologically, lowering the operation temperature is effective to reduce the heat losses of the SOFC stacks and therefore to maintain high efficiency even in smaller systems.

Kyocera adopted the flattened tube design shown in Fig. 2.10. The YSZ electrolyte is fabricated on a cermet anode substrate having gas channels for fuel flow. One side of the anode flattened tube is coated with the  $\text{LaCrO}_3$ -based interconnect. In Fig. 2.10, both sides of the SOFC are shown. These flattened tubes are unique in the sense that they use metals as cell-to-cell connection. This design should be compared with sealless tubular cells by Westinghouse Power Corp., in which the cell-to-cell connection is made with nickel felt. Nickel is thermodynamically stable in a fuel atmosphere so that the adoption of nickel makes it possible to establish stable and effective connection among tubes. In other words, WHPC adopted the cathode-supported tube and made the fuel side as the outer side of the tubes to realize a thermodynamically stable cell-to-cell connection. On the other hand, Kyocera adopted the reverse; flattened tubes were made as anode supported, and, as a result, the cell-to-cell connection should be made on the air side. For this design, therefore, utilization of (non-precious) metal connection becomes the technological key point. In this sense, the lowering of operation temperature is essential.

They built the 1-kW SOFC cogeneration system for residential houses and tested one system in an actual house together with Osaka Gas in 2005 [11]. The start-up time is typically 2 h. A typical result of 24 h operation is shown in Fig. 2.11. During the night, electricity demand is essentially zero except for the refrigerator. Power demand during daytime fluctuates between 500 and



**Fig. 2.11** One day's AC power trend, "Family power demand vs. SOFC power," in the automatic operation mode following the family power demand (under 1 kW) [11]

2500 W. The SOFC system supplies 1 kW, and the rest of the power demand is supplied from grid electricity. The characteristic load-following feature of the cogeneration system is shown in Fig. 2.11. These tests confirm that the system efficiency for a residential house is 43%–48% LHV as an average value for the 24-h test period.

### 2.3.2 Mitsubishi Materials Corporation

Mitsubishi Materials Corporation has developed the SOFC stack/system by using the LSGMC electrolyte. As described earlier, one of the merits of using LSGMC is its high oxide ion conductivity. Although the activation energy of the oxide ionic conductivity of LSGM becomes large with decreasing temperature, and hence the ionic conductivity drops rapidly at lower temperatures, this behavior is improved by Co doping of LSGM. Although the electronic conductivity is also increased by Co doping, the total benefit can be expected from analyses for the deviation from Gibbs energy-based efficiency given in Figs. 2.3 and 2.4 [14].

The high conductivity of LSGMC makes it possible to fabricate self-supported cells and operate them at intermediate temperatures; this in turn makes it easy to fabricate cathode and anode on the LSGMC electrolyte. A sealless stacking method is adopted; electrochemical cells are stacked with metal interconnects using current collectors for cathode and anode sides. Because of this simple configuration and materials, their stack performance is similar to the sum of respective cell performance. In other words, loss in stacking is very small.

As described in a separate chapter, the performance of their 1-, 3-, and 10-kW systems operated around 800°C is quite remarkable, and the systems exhibit high conversion efficiencies. Typical stack efficiency is more than 50% HHV [38]. This result is consistent with the arguments made in Section 2.1 that a strong impact can be expected from the increase in ionic conductivity.

### **2.3.3 *Micro SOFCs by TOTO***

TOTO attempted to fabricate micro tubes in various types. Eventually, they adopted the anode-supported tubular cells with the LSGM electrolyte. The adoption of anode-supported cells much thinner LSGM electrolyte can be used, leading to higher benefits in performance. On the other hand, technological difficulty in the fabrication process becomes more visible to avoid interdiffusion between cell components. Details are also described in a separate chapter of this book.

## **2.4 Perspective**

### **2.4.1 *Applications***

The development of SOFC systems is governed first by materials selection. However, breakthrough by WHPC on the sealless tubular cells indicated that not only materials selection, but also materials processing techniques together with stack design, are inevitably not separable and should be considered together from the early stages of development. In this sense, the main application of WHCP stacks was a stationary power generator for a few hundred kilowatts.

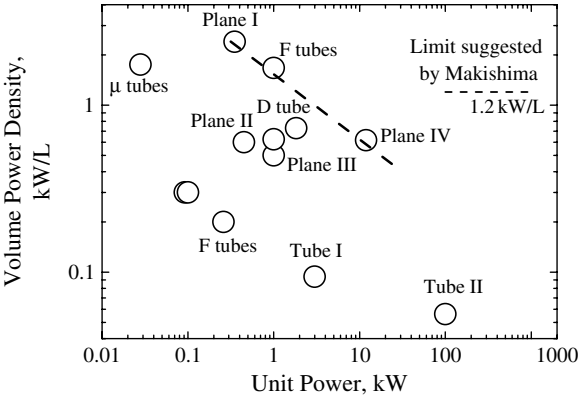
Recent achievement by Kyocera reminds us another aspect of applications: “For what purpose are the SOFC systems applied?” This question is the most important point of the SOFC development. They started with the concept of applications to the residential houses and then selected the operation temperature, plausible cost, and lifetime. On the basis of such system requirements, they started to construct their stacks.

One of their most important achievements is that they demonstrated that a small system can be fabricated and operated as an efficient energy conversion device. There was an argument about the self-thermal sustainability of small SOFC stacks, and it was thought that 1 kW is not sufficient to achieve self-thermal sustainability as well as high conversion efficiency simultaneously. Kyocera has demonstrated that this argument should be made by considering temperature as a parameter, and lowering the operating temperature makes it possible to construct a small but efficient SOFC system. Another impact of the Kyocera system is that they apply the SOFC system to residential houses by

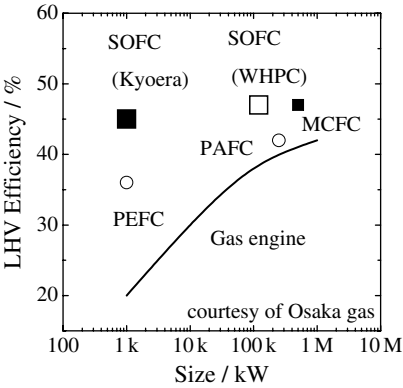
adopting appropriate load-following mode. In gas turbine systems connected to grid electricity, the daily start-and-stop (DSS) operation mode is common, so that whether this DSS operation mode can be applied was thought to be a basic criterion for adaptability of SOFC systems to the electricity market, particularly in Japan. The Kyocera system demonstrates that the DSS operation mode is not necessarily required. Instead, an effective load-following feature can be sufficient for providing power in low-demand periods. In view of this feature, the Kyocera system expands the applicability of SOFC systems not only for nearly steady-state but also for highly transient applications.

In Figs. 2.12 and 2.13, some characteristic features of SOFC stacks and SOFC systems are compared. In Fig. 2.12, the volumetric power density is plotted as a function of stack power. In this evaluation, the gas manifold parts are excluded. It is apparent that high volumetric power density can be achieved in a rather small stack. For tubular stacks aiming at larger systems,

**Fig. 2.12** Comparison of volumetric power density of core stack portion among recently developed SOFC stacks as a function of stack power. A limit of 1.2 kW/l is suggested by Makishima for large continuous chemical reactors such as iron blast furnaces



**Fig. 2.13** Comparison in efficiency among solid oxide fuel cells, polymer electrolyte fuel cells and gas engines as a function of size of generators [Courtesy of Osaka Gas]



the volumetric power density is rather low. However, it should be noted here that the inner portions of tubes can be regarded as paths for introducing air or fuel. For planar stacks, with increasing stack power size, the cell-to-cell distance should be widened to keep the transfer of fuel and air. In Fig. 2.12, a limiting value of 1.2 kW/l is provided for comparison. This limit was proposed by Makishima through considerations on the pattern dynamics on chemical reactors to be operated continuously. For example, the energy density of an iron blast furnace is given in this magnitude. This limiting value tells us that not only the reaction itself but also transport of chemical species to such reaction sites or from those sites is quite important to maintain the continuous chemical reactors. When reactions and mass transfer in fuel cells are compared with the value, the following features should be taken into account:

1. All electrochemical reaction sites are distributed in a two-dimensional manner.
2. All electrochemical reactions and mass transfer phenomena are combined by the electrical chemical path having a three-dimensional network over the entire volume through atomistic reactions. Since electron mobility in metals is much faster than that in ionic species, electron movement in the fuel cell systems leads to a situation where any given reaction site can be connected with the next through electron transport. As a result, the current density distribution is governed by this kind of connection. This is an important difference between fuel cell reactors and normal chemical reactors in which the atomic transport is governed by corresponding reaction rates and mobilities.

These features make it more difficult to construct and operate larger SOFC stacks.

In Fig. 2.13, comparison is made in the system efficiency among various electricity generating systems as a function of system output power. Gas engine systems currently have some market share so that these systems can be regarded as plausible competitors of the fuel cell systems. The most important feature of gas engines is that the efficiency exhibits a strong size dependence. That is, the efficiency of a nearly 1-kW system is as small as 20%, whereas that of a 100-kW system is nearly 40%. Note that the earlier 100-kW SOFC system provided 47% LHV efficiency during a steady-state operation. Because gas engines have the merit of low cost, the cost competition will be quite severe. On the other hand, in a kilowatt size range, difference in efficiency is quite large so that the SOFC systems may have certain merits compared to the inexpensive gas engine systems and also against the PEFC system, which exhibits an efficiency of 32%. In this sense, a 1-kW SOFC cogeneration system can open a new era of development and demonstration of stationary SOFCs.

In 1998, BMW and Delphi proposed to use SOFCs as auxiliary power units (APU). For this purpose, severe requirements such as low volumetric and/or mass-specific power density, rapid start-up times, and stability for frequent thermal cycles should be met. For this purpose, SOFC stacks with novel designs, processing techniques, and materials will be necessary.



### ***2.4.2 Fuel Flexibility and Reliability in Relationship to Intermediate-Temperature SOFCs***

Fuels are important in fuel cell systems. Particularly, hydrocarbon fuels such as natural gas are the most important fuels. Technological issues associated with hydrocarbon fuels are carbon deposition and sulfur poisoning on nickel anodes. Both factors exhibit temperature dependence:

1. Carbon deposition is a result of competition among thermal decomposition reactions of hydrocarbons, reforming reaction with water vapor and electrochemical reactions. By lowering temperature below the decomposition temperature, carbon deposition due to the decomposition ceases, whereas carbon deposition takes place when CO becomes thermodynamically unstable at low temperatures. In this sense, carbon deposition region depends on temperature, composition, and pressure.
2. Sulfur poisoning is particularly important when lowering temperature. The interaction of nickel with sulfur is strong at lower temperatures; that is, solubility of sulfur in Ni increases with lowering temperature and then nickel sulfides can be formed. Actually, Ni cermet anode performance decreases with lowering temperature in the presence of hydrogen sulfide.

Similarly, for certain degradation mechanisms, temperature becomes a dominant factor. Particularly, cathode materials have the tendency of being more reactive to  $\text{CO}_2$ ,  $\text{CrO}_3(\text{g})$ , etc. In view of this, in the intermediate-temperature SOFCs, it becomes important to know degradation mechanisms associated with materials utilized in such SOFCs.

### ***2.4.3 Hybrid Systems***

Recent achievements in the development of intermediate-temperature SOFCs will open a new era even for the hybrid systems combined with gas turbines or other engines. When hybrid systems are designed on the basis of gas turbines, systems will be large and operation temperature will be higher to promote higher efficiencies in the gas turbine side. On the other hand, when a hybrid system is built mainly on fuel cells, smaller size and lower operation temperature will become attractive. Although gas turbine technology has matured, fuel cell technology has just started to evolve so that there is a room for small and low-temperature fuel cells with increased efficiency. Thus, appropriate size and operation temperature for a plausible hybrid systems is still an open issue and will depend on successful development of fuel cells in the near future. For the time being, a MW-size hybrid system is considered to be a typical target.

## 2.5 Summary

Solid oxide fuel cell technology has been reviewed from the point of view of lowering the operation temperatures. This process is closely related with the development of new materials, processing techniques, and stack designs. The most striking fact is that the recent achievement by Kyocera may indicate the start of a new era in the development and demonstration of SOFC systems for stationary applications.

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