NON-REFORMING SOFC WITH HIGH EFFICIENCY

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ABSTRACT

Non-reforming but two-stage-oxidation SOFC has been proposed and analyzed to realize high efficiency on a rather small scale without combination with any turbine system. This SOFC consists of the endothermic electrochemical reaction of hydrocarbons to form carbon monoxide and hydrogen and the exothermic electrochemical reaction of carbon monoxide and hydrogen to form carbon dioxide and water vapor. This can achieve high efficiency without reforming and therefore makes it possible to fabricate those SOFCs which can respond quickly to the load change, can start up and shut down quickly and can be compact enough to be used for transportation use, residential use and co-generation etc. Discussions are made on the materials selection for realizing this SOFC, possible efficiency, technological relationship with the reforming type SOFC or with the direct methane SOFC.

INTRODUCTION

In recent years, the solid oxide fuel cell technology has progressed to confirm the high performance and the long-term stability as power generation system (1) and also to establish the economically accepted fabrication technology based on the wet processes(2,3,4). This means that the technological feasibility of solid oxide fuel cells has been well confirmed and therefore their utilization in various applications has become the main issue. In this context, many proposals have been adanced to obtain the maximum efficiency by combining SOFCs and gas turbines(5,6). This makes it realistic to introduce SOFCs in the power generation systems. On the other hand, application of SOFCs in transportation is still controversial, because the requirements of performance are quite different. For example, quick start is preferable and the high load-following capability is required. In addition, lowering of the operation temperature is required. Although these requirements are severe and difficulties are expected, technologies for overcoming such difficulties will also make the application of SOFCs in power generation more valuable.

The objective of the present investigation is to propose a technological way of meeting these requirements on the basis of our approaches for the direct methane SOFC and related topics(7-11).
Fig. 1  The thermodynamic properties of chemical reactions related to the methane fuel. See text for equations for respective lines.

SMALL SOFC WITH HIGH EFFICIENCY

Background

The main approach for achieving maximum efficiency in SOFCs has focused on the combination of SOFCs with gas turbines on a rather large scale. Actually, many efficiency analyses indicate that possible efficiency will increase with increasing scale of the systems. This is mainly because the total efficiency largely depends on how to utilize those turbine systems which exhibit a large scaling effect. On the other hand, fuel cells themselves do not have a large-scale merit because the electrochemical reaction proceeds through a two (or less) dimensional reaction zone. This in turn suggests that the highly efficient but small system can be realized by using fuel cells alone. This is the basic idea of the present investigation.

As Dokiya et al. (7) already reported six years ago, the main reactions related to the carbonaceous fuels can be divided into the following three reactions;
1) the reforming reaction of carbonaceous fuels (here methane is considered as typical fuel) with water or carbon dioxide to form carbon monoxide and hydrogen.

$$\text{CH}_4 + \frac{1}{3}(2\text{H}_2\text{O} + \text{CO}_2) = \frac{4}{3}(\text{CO} + 2\text{H}_2)$$  (1)

This is an endothermic thermochemical reaction;
2) the partial oxidation to form carbon monoxide and hydrogen:

$$\text{CH}_4 + 0.5\text{O}_2(\text{g}) = \text{CO} + 2\text{H}_2$$  (2)

This electrochemical reaction is endothermic;
3) the oxidation of carbon monoxide and hydrogen to form carbon dioxide and water,
Fig. 2. Change in the energy form for the gas turbine system (a) and for the reforming-type SOFC (b). The theoretical efficiency for the reforming-type SOFC is still much higher than that for thermal engines based on the Carnot cycle.

vapor:

\[
\begin{align*}
\text{CO} + 2\text{H}_2 + 1.5\text{O}_2(g) &= \text{CO}_2 + 2\text{H}_2\text{O} \\
\frac{4}{3}(\text{CO} + 2\text{H}_2) + 2\text{O}_2(g) &= \frac{4}{3}(\text{CO}_2 + 2\text{H}_2\text{O})
\end{align*}
\]  

This is an endothermic electrochemical reaction.

The normal reforming-type SOFC consists of Reactions (1) and (4) and the total reaction is given as the combustion reaction of methane with \( \text{O}_2 \):

\[
\text{CH}_4 + 2\text{O}_2(g) = \text{CO}_2 + 2\text{H}_2\text{O}
\]  

The electrochemical reaction (4) has the tendency that with increasing temperature, the theoretical efficiency (\( \eta = \Delta G/\Delta H \)) decreases, because the heat evolved increase (see Fig.1). In this case, some part of the large exothermic heat will be used for the reforming reaction (1). Fig. 2 shows that the theoretical efficiency for the reforming-type SOFC is higher than those for the thermal engines in which the combustion heat of methane is used as energy source. Note that 30\% of efficiency is lost in combustion. In addition to the high conversion to electricity in fuel cells, the rest of heat can be utilized in turbines to increase the total efficiency.
Fig. 3 Schematic flows of chemicals, heats and electric currents in the Two-Temperature-Two-Stage SOFCs. Cell I is for the partial oxidation of methane, Cell II being for the oxidation of CO and H₂. The exothermic heat at Cell II transfers to Cell I as the endothermic heat.

Proposal of Two-Temperature-Two-Stage (TTT) Solid Oxide Fuel Cells

The efficiency of the solid oxide fuel cells as energy converters is determined in terms of the following three factors;

1) Thermodynamic features of adopted electrochemical reactions; Efficiency is defined as follows

\[ \eta = \frac{\Delta G}{\Delta H} \]  

where the Gibbs energy change, \( \Delta G \), and the enthalpy change, \( \Delta H \), depend on the chemical reaction to be adopted as the total electrochemical reaction.

2) Ways of current collectors and of distributing fuels and oxidants etc.

3) The materials characteristics (Joule loss, overpotential etc).

These will be examined for the present case.

To achieve high efficiency without reforming processes, it becomes essential not to use any thermochemical reaction but use the oxidation reaction of directly introduced methane (7); this can be done by the combination of Reactions (2) and (3). For this case, the total equation again accords with Reaction (5). However, this case has the following important features:

(1) The respective equations are all oxidation reactions so that these chemical reactions can proceed as the electrochemical reaction in the high temperature cells based on the oxide ion conductors.

(2) The endothermic heat of Reaction (2) is about the same as the exothermic heat of Reaction (3). Therefore, by appropriate means for heat transfer, these two reactions
can proceed in the same stack. Since effective heat transfer can be realized by having sufficient temperature difference, it is reasonable to assume that Reaction (2) is done at the lower temperature, Reaction (3) being at the higher temperature. The Gibbs energy change for these two reactions has a temperature dependence so that the two-temperature operations give rise to some lowering in the theoretical efficiency. This is shown in Fig. 4. Note that the temperature dependence of the Gibbs energy is not large so that the corresponding lowering in efficiency is not significant.

There can be several ways of combining two electrochemical reactions in one SOFC stack. One possible way is given in Fig. 5, where a tubular-type cell is adopted. Methane is first partially oxidized by oxygen transported through the tubular electrolyte. This is the lower temperature part. The formed CO and H₂ are then oxidized at the upper part at the higher temperature. Heat evolved at the higher temperature is transferred through the electrolyte and other materials such as nickel and also carried by the gaseous flow. When a stand-alone type SOFC is considered, non-reacted fuel can be burnt to supply heat to the lower temperature cells.

The actual conversion efficiency is governed also by method of current collection and the materials characteristics (the Joule loss, over potentials etc). Here, it should be stressed that even though the present cells are of the two stages, the contribution of the Joule loss and the overpotential to lowering the efficiency appears only once. This can be easily understood in view of the fact that the efficiency of SOFCs can be evaluated as those for an oxygen concentration cell where the oxygen potential at the reducing side is maintained to a low level by fuel. Fig. 5 clearly shows that oxygen goes through the electrolyte only once and that the two-stage oxidation corresponds to the two different oxidation regions where transported oxygen reacts with CH₄ or CO+H₂. This situation makes it reasonable from the efficiency point of view to adopt the two-stage oxidation, although this introduces complicated features of current collection and gaseous distribution.
Applicability of Known Electrolytes

When the operation temperature of electrochemical cells is lowered, usually the conversion efficiency decreases because of increasing resistivity of the electrolyte and increasing overpotential at electrodes. Here, the electrolyte is considered because the numerical treatment can be easily made from available data.

The lowering of the efficiency due to the electrolyte characteristics stems from the resistivity for ionic conduction and also from the oxygen permeation due to non-zero electron conduction (12). These properties can be evaluated for electrolytes whose conductivity of oxide ions, electrons and holes are experimentally determined as functions of temperature and oxygen partial pressure; yttria stabilized zirconia (YSZ) (13), Gd doped ceria (GDC) (14) and lanthanum strontium magnesium gallate (LSGM) (12) are evaluated.

In Fig. 6(a), the efficiency lowering at 1073 K is shown as a function of electrolyte thickness at the current density of 0.3 A/cm². Here, the oxygen potential of the oxidative side is given as in air, whereas that of the reducing side is determined by a mixture of 3 %H₂O and 97% H₂. The lowering in the thicker region is due to the Joule loss; it reflects the magnitude of the ionic conductivity. Note that LSGM has much larger conductivity than YSZ and GDC. The lowering in the thinner region is due to oxygen permeation that is affected by the magnitude of the electron or hole conductivity. YSZ has small electron and hole conductivity. LSGM has rather high hole conductivity, but the lowering in efficiency is not significant. On the other hand, GDC has large electron conductivity and as a result, only 50% of efficiency can be achieved at most.

In Fig. 6(b), the lowering of efficiency is shown as a function of temperature; here, the current density is set as 0.3 A/cm² and two values of electrolyte thickness, 50 µm and 5
Fig. 6 The lowering efficiency in electrolytes due to the Joule loss and the oxygen permeation. (a) $T = 1073\, \text{K}$, $j = 0.3\, \text{A/cm}^2$; (b) $j = 0.3\, \text{A/cm}^2$, $t = 50$ or $5\, \mu\text{m}$. YSZ=$(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$; GDC=$(\text{CeO}_2)_{0.8}(\text{Gd}_2\text{O}_3)_{0.2}$; LAGM=$(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.8}\text{Mg}_{0.2})\text{O}_{2.9}$

$\mu\text{m}$, are adopted. Since the activation energies for the ionic conductivity and the electronic conductivity are different, it can be said that the lowering on the high temperature side is due to the electron(hole) conductivity, that on the low temperature side being the ionic conductivity. Again, LSGM can be used over a wide temperature range without lowering efficiency. YSZ can be used only at higher temperatures. GDC cannot be used because of the significant lowering of efficiency in this electrolyte.

From the above considerations, the following cells can be extracted as possible TTT-SOFCs:

1) YSZ based TTT-SOFCs
Since the normally used Ni/YSZ cermet anode is quite weak against carbon deposition, this anode cannot be used as anode for the partial oxidation reaction (2). We have investigated the tolerance of several anode materials against the carbon deposition and found that a Fe/YSZ cermet anode was stable for more than 200 h in methane diluted with Ar which was partially oxidized to CO and H₂ (8-11). However, this anode is quite weak against the oxidation and degraded at the higher polarization which is needed to oxidize to a full extent. Therefore, in YSZ-based TTT-SOFCs, a normal Ni/YSZ anode can be used in the high temperature cell, whereas a Fe/YSZ anode can be used in the low temperature cell. This configuration is shown in Fig. 5. Since the low temperature region for YSZ is not appropriate as the highly efficient TTT-SOFC, the operation temperature of the low temperature cell should not be lowered too much. This may make it necessary to keep effective heat transfer between cells by using metallic (for example, nickel) materials which thermally connect the two cells, although the current collection will be complicated in such a case. Combustion heat of non-reacted fuel can be also used not to lower the operation temperature on the low temperature side.

2) LSGM based TTT-SOFCs
Since Ishihara et al. (15) already reported that LSGM with Ni anode can be used successfully for the partial oxidation of methane, the same materials can be used for the high and low temperature cells. Since the operable temperature region is widely extended to the lower temperature region, a relatively wide temperature difference can be realized between the two cells to ensure effective heat transfer between the two cells.

When the same anode can be used for both two cells, the stack design becomes easier than the case with use of different anodes. In the latter case, the partial oxidation of methane should be completed before the fuel contacts the high temperature anode. If not, the high temperature Ni/YSZ will be damaged.

COMPARISON WITH REFORMING-TYPE AND DIRECT METHANE SOFCs

Comparison with Reforming-type SOFC
Plausible merits of TTT-SOFCs against the reforming-type SOFCs can be summarized as follows;

1) No thermochemical reactions are introduced so that the high load-following capability can be achieved. The magnitude of response for methane fuel can be expected to be of the same order as that for hydrogen in PEFC fueled with hydrogen.
2) Extension to low temperature operation can be easily made.
3) System becomes simple.
4) Noise level can be significantly reduced (absence of turbine).

In particular, the low temperature behavior is important when compared with the reforming-type SOFC. In the reforming-type SOFC, with decreasing temperature, it becomes more difficult to transfer heat from the cells to the reforming area. In this sense, the reforming temperature is crucial when the lowering of the operation temperature is considered in the reforming type. On the other hand, TTT-SOFCs can be operated at lower temperatures than the reforming temperature; compare the Gibbs energy changes
between Reactions (1) and (2) in Fig. 1. This makes it possible to realize a quick cold start up which is highly required in transportation applications.

Despite above merits, there are many technological difficulties to be surmounted. The most important technology is associated with the control of carbon deposition of methane in gas manifolds or on anodes. In usual fuel processing at high temperatures, steam to carbon ratio is maintained at more than 2 to avoid carbon deposition in any place such as inside pipes made with alloys. This suggests that without excellent method of avoiding carbon deposition, it will be hard to introduce methane directly to fuel cells. On the other hand, since the high temperature cells in TTT-SOFCs can be the same as the reforming-type SOFC, it can be expected that already developed or developing technologies for the reforming-type SOFCs can be easily transferred to that for TTT-SOFCs. In particular, the technology of optimizing stack design to transfer heat effectively from the cells to the reforming area is common and can be easily used in TTT-SOFCs.

**TTT-SOFCs as a Step to Direct Methane SOFC**

The present investigation has revealed that the heat transfer from the high temperature cells to the low-temperature cells for the partial oxidation is important in TTT-SOFCs. This implies that even in direct methane SOFCs, heat transfer will be an essential point. Although the chemical reaction for the direct reaction is one stage as given in Reaction (5) in Fig. 1 and the enthalpy change for this reaction is nearly zero, an actual reaction mechanism might be via the formation of carbon monoxide and hydrogen. In such a case, the electrochemical reaction becomes essentially the same as that in TTT-SOFCs. Thus, the heat transfer becomes crucial even in direct methane SOFCs. In this sense, TTT-SOFCs can be regarded as a step to the development of direct methane SOFCs. In particular, LSGM based TTT-SOFCs can be set up by using the same materials throughout the stack and therefore it is a good example to understand the cell characteristics for the stand-alone type SOFC.

When the direct electrochemical reaction of methane without forming carbon monoxide or hydrogen could be established, it will not be necessary to transfer heat inside stacks. This will be an ideal stand-alone type SOFC. To realize it, reaction mechanism of the direct methane SOFC should be extensively investigated in the future.

**CONCLUSIONS**

The present investigation has indicated that as the stand-alone type SOFC, the two-temperature-two-stage SOFC has several merits against the reforming-type SOFC. The technological difficulties are also expected in handling dry methane.
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