MATERIALS FOR CLEAN ENERGY CONVERSION

Harumi Yokokawa

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki, Japan

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Contents

Summary

The conversion efficiency is analyzed for the combustion process for turbines and the electrochemical process for fuel cells. In turbines, lowering of efficiency inevitably takes place on combustion process and during cooling to the inlet gas temperature. On the other hand, the conversion efficiency of fuel cells is determined by the

electrochemical reaction to be adopted, internal ohmic resistance, and overpotentials. By combining two processes, the conversion efficiency can be maximized and therefore reduce the emission of CO_2. Use of oxygen instead of air in fuel cells and turbines makes it easy to separate CO_2 from reacted gases consisting of CO_2 and water.

To maximize the actual efficiency in fuel cells, materials characteristics become crucial, because the main lowering of efficiency occurs in overpotentials of electrodes and internal ohmic resistance in electrolyte. Furthermore, materials science plays an important role in establishing the fuel cell technology because the materials requirements for fuel cell components are severe and to meet with those requirements, a systematic approach is needed. The thermodynamics is useful for understanding the performance of high-temperature solid oxide fuel cells. In particular, stability/reactivity analyses can be made in a systematized way in terms of the valence stability and the stabilization energy for double oxides. As an example, the materials behavior of the interface between lanthanum strontium manganite and yttria stabilized zirconia was analyzed in terms of the reducing processes of manganese dissolution in YSZ and the oxidizing processes of the $La_2Zr_2O_7$ formation and of the zirconium dissolution in perovskite.

1. Introduction

Since the first use of fires in our history, the utilization of energy has been essentially based on the use of fire. In other words, combustion of fuels has been used as sources for electrical and other driving powers. Thus, the combustion and utilization of resulting heats have been an important technology and this led to the establishment of the modern science based on thermodynamics.

In recent years, the direct conversion between chemical energy and electricity has attracted much attention. For such a purpose, the electrochemical processes are used instead of combustion. Fuel cells (FCs) are for conversion from chemical energy to electricity, and electrolyzers are to use electricity for production of chemicals. Whereas electrolysis has been well established and used successfully on an industrial scale, fuel cells have not been realized except for special purposes such as space applications. The basic idea of fuel cells had been already proposed more than hundred fifty years ago. Difficulties of realizing fuel cells can be ascribed mainly to the fact that materials requirements are severe; in addition to requirements for electrochemical properties, the prospective materials have to exhibit the high chemical stability in severe chemical environments such as acidic conditions. This has made it difficult to develop materials which can meet the requirements within appropriate materials/fabrication costs. Even so, advances in modern materials science, including materials thermodynamics, make it possible to develop such materials that can tolerate the stringent conditions of service and can be fabricated with sufficiently low cost. This provides the prospect for the full utilization of fuel cells in many application field, such as residential use, transportation, cogeneration of heat and electricity, industrial use, and so on.

2. Comparison between Combustion Processes and Fuel Cells for Energy Conversion

2.1. Combustion Process related to Heat Engines

In order to utilize fuels effectively and to reduce CO_2 emissions, it is essential to have an understanding of the various processes taking place and determine how the efficiency of energy conversion may be improved. This can be made by analyses on flows of energy. Since energy conservation is always satisfied, flows of energy can be drawn to show how the form of energy (chemical, heat, electrical, etc) changes during processes. The quality of respective energies can be defined from their ability to do work. For example, heat at a high temperature can do work more than the same amount of heat at a lower temperature. This is formulated as the Carnot efficiency. For chemical energy, the Gibbs energy gives the maximum energy that can be converted to work under isothermal conditions. To combine the effects of heat and chemical energy, the thermodynamic function termed "exergy" is used in many cases.

Figure 1 shows a schematic flow of normalized effective energy for power generation by the combustion of methane. The important features can be summarized as follows;

1. The quantity of chemical energy can be defined as the enthalpy change for the combustion reaction at room temperature. These energies can be used at least as heats. This is the starting point. As a measure of the ability of energy conversion from chemical energy, the Gibbs energy instead of the enthalpy change should be used because the amount of work to be extracted is less than the Gibbs energy values.

2. On combustion, 20-30% of exergy will be lost as shown in Figure 1. After conversion to heat, the ability of doing work can be counted as thermal energy which is characterized in terms of the Carnot efficiency. When the ambient temperature is used as a low temperature heat sink, the Carnot efficiency can be determined from a combustion temperature alone. When air is used as oxidant, a typical adiabatic combustion temperature of natural gases is roughly 2500 K.

3. On transfer of the heat from combusted gases to thermal engines (gas turbines or steam turbines), there is a decrease in the Carnot efficiency because of the decrease in temperature without doing work.
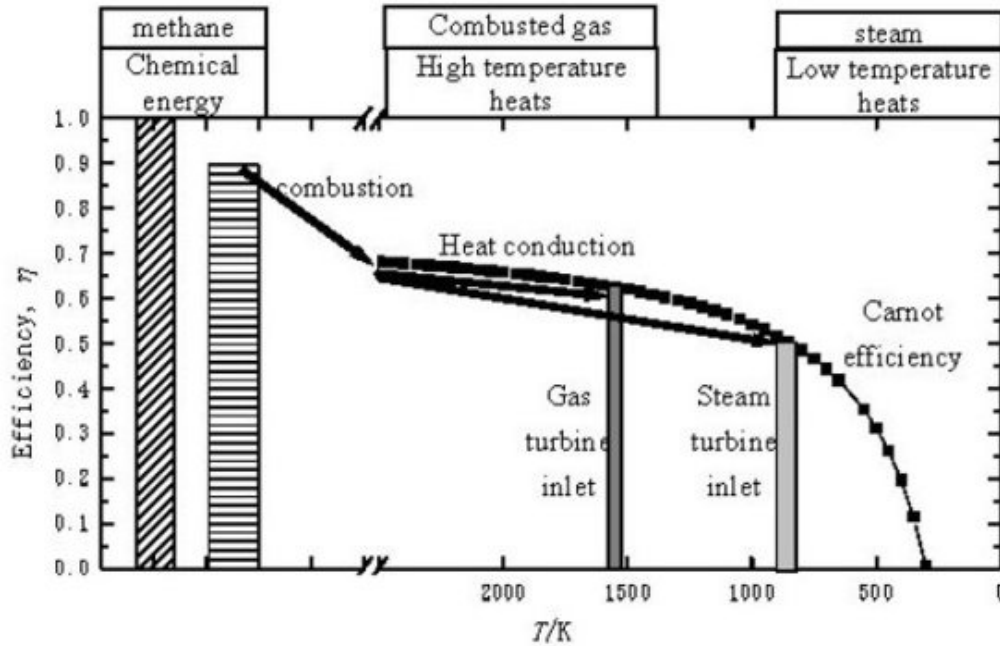
Figure 1. Flow of normalized effective energy (exergy) in methane combustion. The initial value is adopted as the enthalpy change for combustion to CO_2 and water and to CO_2(HHV); all values are normalized to this value. The exergy of methane is counted here as the Gibbs energy change to CO_2 and steam (horizontally shaded bar). The dotted line (full squares) is the Carnot efficiency normalized for the initial chemical energy of methane and plotted as a function of temperature. The plausible inlet temperature of gas turbine and steam turbine is shown. The actual efficiency of gas turbine/steam turbine cannot proceed the Carnot efficiency at the respective inlet temperature.

Since heat loss can take place anywhere in the system, actual conversion efficiency will be lower than that shown in Figure 1. After determining the reasons for such exergy loss, the important strategy for improving the efficiency can be derived as follows;

1. Increase the scale of heat engines: This reduces heat loss during the thermal processes.
2. Increase the operation temperature of heat engines: This can be achieved by the following ways; (a) operation of steam turbines under super critical state, (b) use of gas turbines whose operational temperature is higher than that of steam turbines, (c) combination of gas turbines and steam turbine, (d) increase the operational temperature by developing ceramic gas turbine.
3. Introduction of fuel cells.
4. The third strategy is the most fundamental technological challenge in utilization of energy in a sense that no combustion process is involved in fuel cells.

2.2. Principle of Fuel Cells

When a chemical reaction takes place via mobile ions in an electrolyte, the chemical energy (Gibbs energy) associated with the reaction can be extracted as electricity. Here, the oxidation of hydrogen with oxygen is considered. Two different cases are shown in Figure 2; that is, one is for use of proton conductive electrolyte in low temperature fuel

cells, the other being of oxide ion conductive electrolyte in high temperature fuel cells.
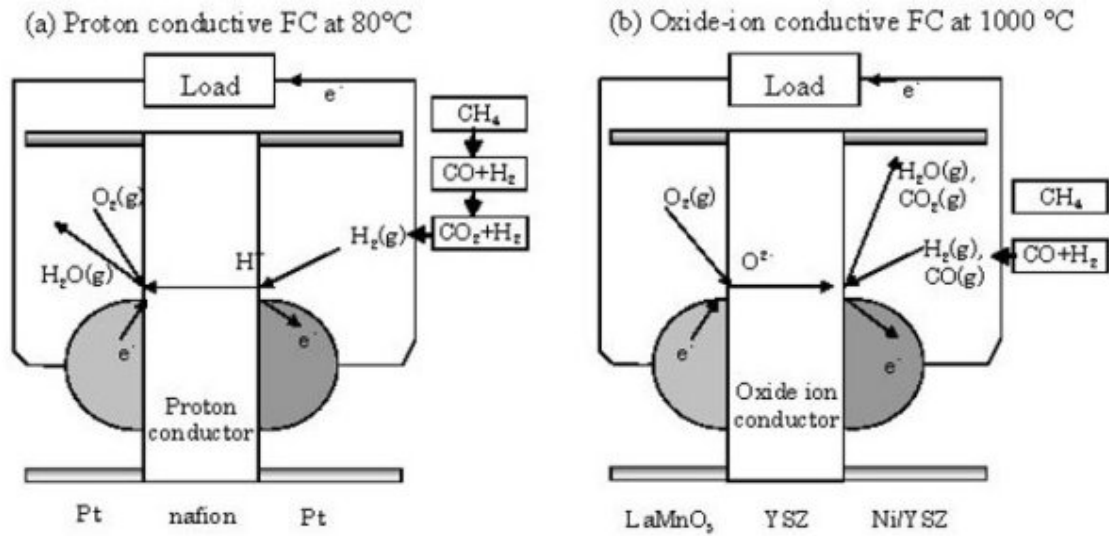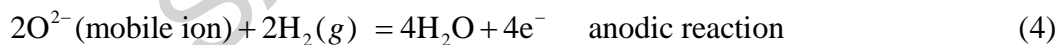

Figure 2. Principles of fuel cells for two typical cases. (a) Fuel cells with proton conductor as electrolyte; (b) fuel cells with oxide ion conductor as electrolyte. When fuels other than H_2 are used, different features appear in fuel processing and heat management.

The relevant electrochemical reactions are as follows;

(1) Case 1

$$4H^+ \text{ (mobile ion)} + O_2(g) + 4e^- = 2H_2O \qquad \text{cathodic reaction} \qquad (1)$$

$$2H_2(g) = 4H^+ \text{(mobile ion)} + 4e^- \qquad \text{anodic reaction} \qquad (2)$$

(2) case 2

$$O_2(g) + 4e^- = 2O^{2-} \text{(mobile ion)} \qquad \text{cathodic reaction} \qquad (3)$$

$$2O^{2-} \text{(mobile ion)} + 2H_2(g) = 4H_2O + 4e^- \qquad \text{anodic reaction} \qquad (4)$$

(3) total reaction

$$2H_2(g) + O_2(g) = 2H_2O \qquad (5)$$

The total reaction Eq.[5] is the same for two cases.

2.3. Conversion Efficiency of Fuel Cells

The ideal conversion efficiency for fuel cells, η^{TH}, is defined as

$$\eta^{TH} = \frac{\Delta G}{\Delta H} \tag{6}$$

where ΔG and ΔH are the Gibbs energy change and the enthalpy change, respectively, for the electrochemical reaction. This efficiency therefore depends on the electrochemical reactions occurring in the fuel cells. Usually, heat generated in a normal chemical reaction can be characterized in terms of the enthalpy change for the reaction, $-\Delta H$. In fuel cells, the quantity corresponding the Gibbs energy is extracted as work so that the quantity, $-(\Delta H - \Delta G) = -T\Delta S$, ecomes the measure for whether the electrochemical reaction becomes endothermic or exothermic.

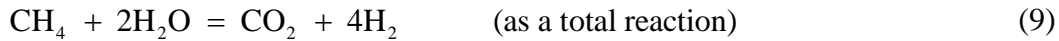| Reactions	$\Delta_r H°$ (298) kJ mol^{-1}	$\Delta_r G°$ (298) kJ mol^{-1}	$\Delta_r S°$ (298) JK^{-1}mol^{-1}	η (350 K)	η (1250K)
$H_2(g) + 0.5O_2(g) = H_2O(g)$	-241.8	-228.6	-44.4	0.93	0.72
$CO + 0.5O_2 = CO_2$	-283.0	-257.2	-86.5	0.89	0.62
$CH_4 + 2O_2 = CO_2 + 2H_2O(g)$	-802.4	-800.8	-5.1	1.00	1.00
$CH_4 + 0.5O_2 = CO + H_2$	-35.7	-86.4	170.0	2.81	12.40

Table 1. The thermodynamic characteristics for possible fuel cell reactions and theoretical conversion efficiency at low and high temperatures.

In Table 1, the main characteristic features of fuel cell reactions are listed. Oxidation of carbon monoxide exhibits similar features to oxidation of hydrogen. With increasing temperature, the efficiency decreases because of negative entropy change. The complete oxidation of methane has essentially zero entropy change and therefore, the efficiency is nearly equal to unity. On the other hand, the partial oxidation of methane to hydrogen and carbon monoxide has a positive entropy change. When this reaction is used, an endothermic effect takes place. The theoretical conversion efficiency becomes more than unity. In other words, heats (at least some parts of heat) can be converted to work during the electrochemical partial oxidation of methane. This feature is completely different from the normal heat engines. This means that fuel cells are free from the limitation by the Carnot efficiency and will provide a new possibility of using heat in electrochemical reactions to obtain more efficient use of energy resources.

2.4. Use of Natural Gases

Since the low temperature fuel cells can use only hydrogen as fuels, methane or other carbonaceous fuels have to be converted to hydrogen.

$$CH_4 + H_2O = CO + 3H_2 \qquad \text{(reforming reaction)} \tag{7}$$

$$CO + H_2O = CO_2 + H_2 \qquad \text{(shift reaction)} \tag{8}$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \qquad \text{(as a total reaction)} \qquad (9)$$

This reaction proceeds endothermically around 850°C so that more than 20% of produced hydrogen has to be consumed to supply the heat. For this reason, the fuel utilization of the low temperature FCs is usually limited to around 70% and the rest of the fuel will be used in the above reforming process.

For high temperature fuel cells, the direct oxidation of methane is of interest because of its high theoretical conversion efficiency. Unfortunately, however, no good anodes have been developed because of difficulties of avoiding carbon deposition in dry or slightly humid atmosphere. Instead, reforming of CH_4 with H_2O is adopted to obtain CO and H_2 that can be reacted on the high temperature anodes. Since the SOFC operating temperature (1000°C) is higher than that for the reforming temperature (700°C), outlet heats from SOFCs can be used for the reforming process. This gives rise to the important difference from the low temperature fuel cells.

2.5. Characteristic Features in Utilization of Fuel Cells

In utilization of fuel cells, the following merits are expected:

1. There can be a variety of applications of fuel cells; the centralized large power plant in a several 100 MW size to small version in a few kW size for residential use. Application in transportation is also of potential importance.
2. Since power generation can be made not only in centralized large power generation plants but also in decentralized places, heats can be utilized in effective ways.
3. Total efficiency of utilization will be increased so that the CO_2 emission will be reduced. Since reacted gases consist of water and carbon dioxide, it will be easy to separate CO_2 from the reacted gases. For this purpose, pure oxygen instead of air has to be used to burn the rest of the fuel.
4. In many cases, sulfur will be removed from the fuels before utilization in fuel cells. This makes emission of sulfur oxide low.
5. Chemical reactions can be controlled more easily compared with combustion. In other words, reactions can proceed at relatively low temperatures so that emission of nitrogen oxides can be avoided even when gas turbines are combined.
6. Noise can be maintained to an extremely low level.

On the other hand, there are several disadvantages of fuel cells:

1. Processing is required for the fuels for the respective fuel cells. In addition, impurities should be maintained to low levels.
2. Except for pure hydrogen fuel in the low temperature FCs, 100% fuel utilization cannot be achieved because fuels always coexist with other gases such as CO_2 and H_2O.

The second deficiency can be overcome by combining high temperature fuel cells and gas turbines; outlet gas from fuel cells can be completely combusted to provide high temperature gases to turbines. This is one example of how to increase the total efficiency by optimizing the utilization of electricity and heats in various configurations

of fuel cells and turbines.

3. Materials Requirements as Electrochemical Energy Converters

The practical conversion efficiency of fuel cells is determined also by materials characteristics such as internal ohmic resistance in electrolyte and interconnect materials and by overpotentials in electrodes.

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Biographical Sketch

Harumi Yokokawa

Nationality : Japan;

Place of birth : Saitama, Japan

Date of birth : 8 May 1948.

Education: the department of nuclear engineering, faculty of engineering, University of Tokyo,

Bachelor of Engineering, April 1972

- Doctor of Engineering, March 1977
- Job
- April 1977 joined with the National Chemical Laboratory for Industry
- October 1978- June 1980

Research Associate, the James Franck Institute, University of Chicago,

April 1982 Senior researcher

January 1993, NCLI together with other three laboratories was reorganized to the National Institute of Materials and Chemical Research. At present, Group leader of Energy related materials Group.

Awards

- The Award from JICST (Japan Information Center for Science and Technology, 1989)
- The Award for Tsukuba Chemistry and Biology, 1997
- The Award from the Agency of Science and Technology, 2000.