Equilibria in Fuel Cell Gases

K. Sasaki and Y. Teraoka
Kyushu University, Interdisciplinary Graduate School of Engineering Sciences
Kasuga-shi, Fukuoka 816-8580, JAPAN
(sasaki@mm.kyushu-u.ac.jp)

Fuel cells have been increasingly accepted as environmentally compatible, efficient energy conversion systems. In particular, SOFCs may be regarded as the most flexible fuel cells in respect to their flexibility in selecting the types of fuels able to be supplied directly to the fuel electrodes.

Fuel gases including hydrocarbons and alcohols are either directly supplied or reformed in a reformer before supplying to fuel cells. In order to apply such fuel gases, it is in particular essential to know the gas compositions in thermodynamic equilibrium under given operational conditions for any types of fuel cells. In the case that reforming and/or decomposition kinetics are sufficiently fast, the compositions of the fuel gases are identical to those in thermodynamic equilibrium. Thermochemical calculations will give such information for any kinds of fuel gases if their thermochemical data are available. As possible fuels, following species have been taken into account: natural gas (consisting mainly of CH_4 with a small amount of other hydrocarbons such as C_2H_6), coal gas (consisting mainly of CO and H_2), liquefied petroleum gas (LPG, consisting mainly of C_3H_8 with C_4H_{10}), naphtha (consisting mainly of C_5 and C_6 hydrocarbons), gasoline (consisting mainly of hydrocarbons with carbon numbers around 8), kerosene (consisting mainly of hydrocarbons with carbon numbers around 12), alcohols, biogas, and coke oven gas.

Thermochemical calculations were carried out using a program, HSC chemistry (Version 4.0, Outokumpu Research Oy, Finland) with an extensive thermochemical database. In the present study, the thermochemical data of ca. 300 compounds with carbon numbers of 4 or less and, in addition, possible fuel species such as higher alkanes were taken into account. The calculations were performed by assuming a reactor to which a (mixed) fuel gas normalized to 1 kmol carbon was supplied, and the amounts of gas, liquid, or solid products in thermodynamic equilibrium were numerically derived, in the temperature range between 100^o and 1000^{o}C in a step of 10^{o}C

Figure 1 shows the equilibrium products for methane- and methanol-based fuels with the steam-to-carbon ratio of 1.5. It can be found that the carbon deposition can be neglected within the wide temperature range. The calculation results for other fuels mentioned above are shown elsewhere [1].

Minimun amounts of H_2O essential to prevent carbon deposition were calculated, and the results are shown in Fig. 2 for hydrocarbons. While S/C of 1.5 is enough for CH_4, higher S/C is needed with increasing carbon number of hydrocarbons. We have also made similar calculations for O_2 (partial oxidation) and CO_2 (reforming) [1].

It has been found that the major constituents in fuel gases are H_2(g), H_2O(g), CO(g), CO_2(g), CH_4(g), and C(s). Since their compositions depend solely on the C-H-O ratio, we can plot, on such C-H-O diagrams, parameters relevant to operational conditions, including carbon deposition region, gas partial pressures, and electromotive force. As examples, carbon deposition region at temperatures between 100 and 1000^{o}C is shown in Fig. 3. Various other ternary diagrams are reported elsewhere [1].

1) K. Sasaki and Y. Teraoka, *J. Electrochem. Soc.*, submitted.

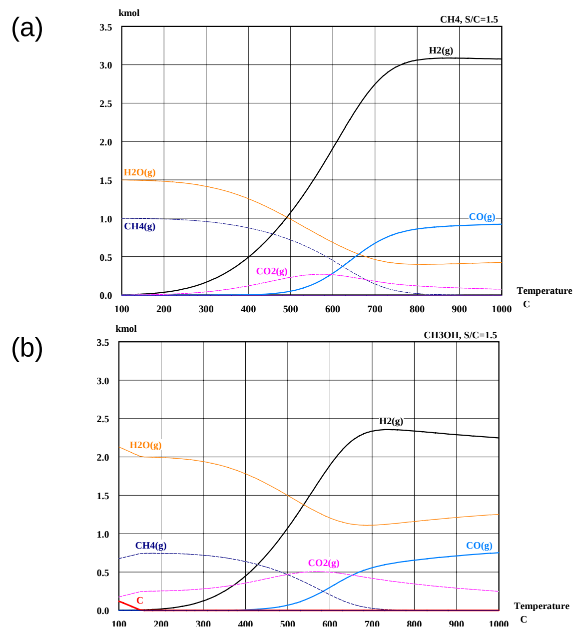

Fig. 1: Equilibrium products from (a) methane-and (b) methanol- based fuels with the steam-to-carbon ratio of 1.5.

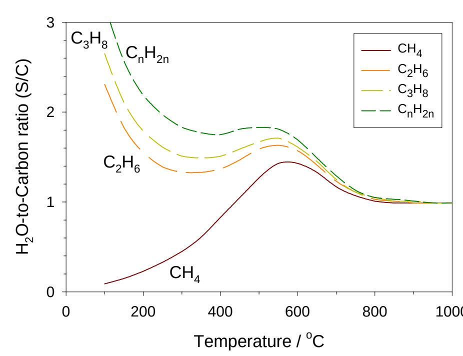

Fig. 2: Minimum steam-to-carbon (S/C) ratio needed to prevent carbon depositions in thermodynamic equilibrium for hydrocarbons.

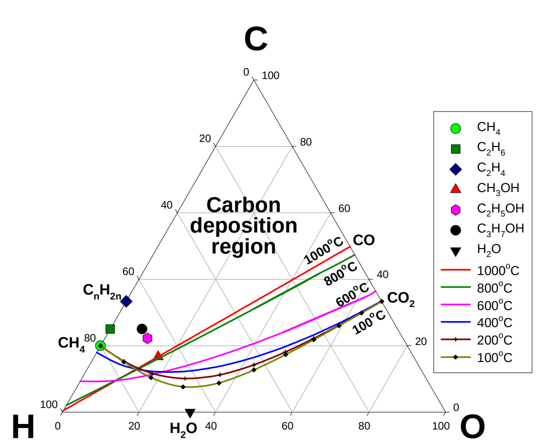

Fig. 3: Carbon deposition limit lines at various temperatures in the C-H-O diagram.