EQUILIBRIA IN FUEL CELL GASES

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ABSTRACT

Thermochemical calculations have been performed to derive equilibrium products and their compositions in the temperature range between 100° and 1000°C for various possible SOFC fuels including natural gas, liquefied petroleum gas, gasoline, kerosene, alcohols (methanol, ethanol, propanol), dimethyl ether, biogas, and coke oven gas. The minimum amounts of steam and oxygen to prevent carbon deposition are derived. The carbon-hydrogen-oxygen (C-H-O) ternary diagrams have been constructed, describing relevant operational conditions such as carbon deposition region, electromotive force, and gas partial pressures.

INTRODUCTION

Solid oxide fuel cells can be regarded as the most fuel flexible of the various types of fuel cells. SOFC fuels may not only include H₂ and CO but also hydrocarbons, alcohols, and other fossil, renewable, and/or recycled energy resources, as illustrated in Figure 1. In order to reveal the optimum operational conditions for a given fuel, equilibrium fuel gas composition is relevant to be known (1-3). Equilibrium compositions are those in which decomposition and reforming reaction kinetics are fast enough to reach thermodynamic equilibrium. Power generation characteristics of SOFCs operated with a given fuel can therefore be understood as (i) those operated with the corresponding fuel gas in complete thermodynamic equilibrium, and (ii) effect of the deviation of real fuel gas composition from the equilibrium composition. In this study, we focus on the former issue (i). The aim of this study is therefore to analyze equilibria in fuel cell gases in a wide temperature range of interest for various types of fuels.

As initial fuel species, considered are natural gas (consisting mainly of CH₄ with a small amount of other hydrocarbons such as C₂H₆), liquefied petroleum gas (LPG, consisting mainly of C₃H₈ with C₄H₁₀), gasoline (consisting mainly of hydrocarbons with carbon numbers around 8), kerosene (consisting mainly of hydrocarbons with carbon numbers around 12), alcohols, dimethyl ether, biogas (consisting mainly of CH₄ and CO₂), and coke oven gas (consisting mainly of H₂, CH₄, and CO). Thermochemical calculations have been demonstrated to be useful, e.g. for fuel cell materials development (4), for
studies on interfacial electrochemical properties (5), and for point defect engineering of fuel cell related materials (6,7). The latter issue (ii) is discussed in our separate paper in this proceeding (8).

For realizing flexible fuel cells

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**Figure 1. Possible SOFC Fuels.**

**CALCULATION PROCEDURE**

Thermochemical calculations were carried out using a program, HSC chemistry (Version 4.0, Outokumpu Research Oy, Finland) with an extensive thermochemical database (9-11). In this 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° and 1000°C in a step of 10°C. The amounts of each product (chemical compositions) in thermodynamic equilibrium were derived as those at which the total Gibbs energy of the mixed products had been minimized. The total pressure was 1 bar. Details are given in Ref. 3.

**RESULTS AND DISCUSSION**

**Equilibrium Products (Compositions)**

As the equilibrium products can be in gas state and/or in solid state (graphite) at elevated temperatures, most of the results calculated in the following are shown as the amounts of products rather than concentrations. Figure 2 shows the equilibrium products from methane- and methanol-based fuels for the steam-to-carbon ratio (S/C) of 1.5. Figure 2(a)
for the methane-based fuel shows that the equilibrium gas is rich in CH4(g) and H2O(g) at lower temperatures, while it is rich in H2(g) and CO(g) at higher temperatures. No solid graphite will be formed at this S/C. Figure 2(b) reveals that carbon deposition is thermodynamically expected for the methanol-based fuel but only below 140°C. In addition, the amount of H2O(g) formed from the methanol-based fuel shown in Figure 2(b) is much larger than that from the methane-based fuel shown in Figure 2(a). This feature can be understood since alcohols can be regarded as hydrated hydrocarbons.

As the carbon formation becomes significant especially for higher hydrocarbons (8,12), an addition of e.g. H2O may be helpful to prevent carbon deposition. Figure 3 shows the equilibrium products at the S/C of 3.5 for C3H8 (propane), C8H18 (n-octane), and C12H26 (n-dodecane) simulating petroleum gas, gasoline, and kerosene, respectively. We can clearly find that no carbon formation is expected for any hydrocarbons (alkanes) even for C12H26. This result indicates that, from the thermodynamic viewpoint, the S/C of 3.5 is, at least, enough to prevent carbon deposition. The major dependency on carbon number is a decrease in the amount of H2(g) with increasing carbon number.

As thermochemical calculations can be applied to any types of possible fuel cell fuels, we can demonstrate such calculations also for other hydrocarbons and for more complicated mixed gases. For example, Figure 4 shows the equilibrium products from (a) dimethyl ether (CH3OCH3) mixed with H2O (S/C=1.5), and (b) biogas and (c) coke oven gas in typical compositions. Dimethyl ether with the boiling temperature of -24.8°C has advantageous as a gaseous fuel under ambient conditions while it can be easily liquefied compared to methane. The use of biogases may enable us to realize a renewable total energy system with fuel cells. The use of coke oven gas may improve energy efficiency, e.g. in steel manufacturing plants due to a higher efficiency of fuel cell-based power generation.

Figure 4(a) shows that the amounts of equilibrium products (and thus the compositions) from the dimethyl ether-based fuel were identical to those from the ethanol-based fuel for the same S/C (1-3). This is simply because the ratios among C, H, and O for both fuels are identical. For biogas as shown in Figure 4(b), significant carbon deposition at lower temperatures is expected so that an addition of H2O is essential to prevent the deposition. On the other hand, the amount of carbon deposited becomes smaller with increasing temperature so that the equilibrium gas is rich in H2(g) and CO(g) at higher temperatures. In the case that the coke oven gas is directly supplied to SOFCs (see Fig. 4(c)), an addition of H2O is also essential to operate fuel cells without carbon formation. Contrary to the biogas, a significant carbon deposition from the coke oven gas is expected at higher temperatures. As both mixed gases mainly consist of H2(g) and CO(g), SOFCs are attractive since they can directly use CO as a fuel. These examples clearly indicate that equilibrium compositions and temperature region of the carbon deposition vary considerably with the types of fuels applied.
Figure 2. Equilibrium products from (a) methane-and (b) methanol-based fuels with the steam-to-carbon ratio of 1.5.
Figure 3. Equilibrium products from alkane-based fuels with the steam-to-carbon (S/C) ratio of 3.5: (a) propane ($C_3H_8$), (b) n-octane ($C_8H_{18}$), and (c) n-dodecane ($C_{12}H_{26}$).
Figure 4. Equilibrium products from (a) a dimethylether-based fuel with the steam-to-carbon (S/C) ratio of 1.5, (b) a typical biogas (CH₄ 55%, CO₂ 30%, and H₂O 15%) and (c) a typical coke oven gas (H₂ 53%, CH₄ 30%, CO 7%, N₂ 4%, C₂H₄ 3%, CO₂ 3%).
Fuel Processing Conditions for Hydrocarbons and Alcohols

The addition of H₂O, O₂, or CO₂ to hydrocarbon-related fuel gases enables the prevention of carbon deposition while too high a concentration of these species in the fuel gases results in an increase in oxygen partial pressure and thus a decrease in cell voltage. Therefore it is of technological relevance to know their minimum amount essential to prevent carbon formation expected from thermodynamic equilibrium. It should be noted, however, that carbon deposition could occur at a higher concentration of these co-reactants due to kinetic reasons.

![Graph](image)

**Figure 5.** Minimum steam-to-carbon (S/C) ratio needed to prevent carbon deposition in thermodynamic equilibrium for (a) hydrocarbons and (b) alcohols.

Figure 5 shows the minimum S/C needed to prevent carbon formation for various (a) hydrocarbons and (b) alcohols. For methane, the S/C of 1.5 is sufficient enough to prevent carbon deposition within the whole temperature range studied, mainly because CH₄ is stable at lower temperatures. With increasing carbon number of hydrocarbons, higher S/C is needed, approaching the values for C₅H₂₆ with a sufficiently high n value. In addition, a higher S/C becomes needed with decreasing temperature, with a maximum around 500°C.

Among various alcohols shown in Figure 5(b), no H₂O addition is needed for CH₃OH at a high temperature e.g. 1000°C. However, more H₂O is needed with decreasing temperature, again with a maximum around 500°C. These tendencies are common for alcohols. Also higher S/C is needed with increasing carbon number of alcohols, again approaching the values for C₅H₂₆. Note however that S/C can be optimized by taking the kinetic rate of carbon formation at low temperatures into account.

An addition of O₂ instead of H₂O is also useful to reform fuel gases. This partial oxidation, often made with a catalyst, is practical without supplying a large amount of water but associated with a decrease in efficiency. Figure 6 shows the minimum amounts of O₂ needed for the partial oxidation to prevent carbon formation in thermodynamic
equilibrium. These lines denote the lower limits of the $O_2$-to-carbon ratio required. Note that too high an $O_2$-to-carbon ratio leads to too high an oxygen partial pressure. Indeed, to obtain the oxygen partial pressure of $10^{-10}$ bar the required $O_2$-to-carbon ratio was 2.0 for $CH_4$, 1.5 for $CH_3OH$, and 1.5 for $C_nH_{2n}$, above which the gas supplied can no longer act as fuel cell gases. Therefore these values act as the upper limits for the partial oxidation of hydrocarbons and alcohols.

![Figure 6](image)

**Figure 6.** Minimum $O_2$-to-carbon ($O_2/C$) ratio needed to prevent carbon deposition in thermodynamic equilibrium for (a) hydrocarbons and (b) alcohols.

Figure 6(a) clearly shows that the dependence on carbon number of hydrocarbons is almost identical within the wide temperature range, except at lower temperatures below ca. 300°C. On the other hand, alcohols contain oxygen in the molecules. Figure 6(b) clearly reveals that $CH_3OH$ thus requires a less amount of $O_2$, compared to $CH_4$. With increasing carbon number of alcohols, the amount of $O_2$ required increases and approaches the values for $C_nH_{2n}$. This relation can be easily understood as the number of carbon and hydrogen per oxygen in these molecules increases.

**Carbon-Hydrogen-Oxygen (C-H-O) Ternary Diagrams**

The thermochemical calculations have revealed that the major constituents of equilibrium products are $H_2(g)$, $H_2O(g)$, $CO(g)$, $CO_2(g)$, $CH_4(g)$, and solid graphite, while the concentrations of various hydrocarbons and alcohols are much lower. Furthermore, it has been revealed that the concentrations (and the partial pressures for ideal gases) of various gaseous species can be specified by the C-H-O ratios (1-3). This fact indicates that various operational conditions including gas partial pressures, carbon deposition region, and electromotive force can be presented in the C-H-O diagrams. Ternary diagrams have been widely used e.g. to describe phase diagrams (13,14). The position of any compound lies within this triangular coordinate system, where each corner of the triangle represents one of the three components, C, H, and O in this case.

The positions of various hydrocarbons and related species are shown in Figure 7. These hydrocarbon-related species have been considered as possible fuel cell fuels (12,15-22) via an external or internal reforming. The positions of (gaseous) species such as $H_2$, $H_2O$, 

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O₂, CO, and CO₂ are also shown in the figure. Alkanes including CH₄, C₂H₆, and C₃H₈ can be found on the C-H axis. Alcohols including CH₃OH, C₂H₅OH, and C₃H₇OH can be found on the line between the positions of H₂O and CₙH₂ₙ. The positions of various hydrocarbon-related species such as dimethyl ether, ethylene glycol, formaldehyde, formic acid, and toluene are also specified in the figure. The positions of mixed fuel gases, biogas and coke oven gas in typical compositions, are also shown as examples. The figure indicates that most of these species are hydrogen-rich with carbon in a minor content, and they contain oxygen in various fractions depending on the degree of oxidation and/or hydration.

As carbon deposition is one of the major problems to be prevented when hydrocarbon-related fuel gases are used, it is very helpful to reveal the carbon deposition region in the C-H-O ternary diagram (1-3, 12, 23). Once the ratio among these three components is determined, we can know if carbon formation occurs in non-negligible amount by assuming complete equilibria. The boundaries of the carbon deposition region have been calculated and the results are shown in Fig. 8 for various temperatures between 100° and 1000°C. These lines correspond to an equilibrium quantity of solid graphite equal to 10⁻⁶ of the carbon initially present in the fuel.

According to Figure 8, carbon formation can be predicted when the position of a fuel with a given C-H-O ratio is within the region, i.e., on the carbon rich side of the boundary lines. At 1000°C, no carbon deposition is expected if the carbon-to-oxygen ratio is less than unity. Since the positions of various (pure) hydrocarbons lie within the deposition region, a sufficient addition of H₂O, O₂, and/or CO₂ is needed to prevent the deposition. With decreasing temperature, we can find that (i) the deposition region expands deeply into the carbon poor region, and (ii) the boundary line approaches from the position of H₂ and CO to that of CH₄ and CO₂.

These thermochemical calculations simultaneously give the concentrations of all species, for which the thermochemical data are taken into account, including pO₂. Figure 9 shows the electromotive force (the theoretical open circuit voltage) for a fuel cell (a concentration cell) constructed with air (pO₂=0.205 bar) as an oxidant on the cathode side (a) at 1000°C and (b) at 600°C. In Figure 9(a), it can be observed that the electromotive force changes with the hydrogen-to-oxygen ratio within the carbon deposition region.

Outside the deposition region, the theoretical open circuit voltage decreases with increasing H₂O (steam reforming), O₂ (partial oxidation), and/or CO₂ (CO₂ reforming) content. Near the straight line between the position of H₂O and the position of CO₂, the electromotive force changes drastically. The gas is no longer useful as a fuel cell gas on the oxygen-rich side of this line. These results indicate that the trapezoidal region with its apexes specified by the positions of H₂, H₂O, CO, and CO₂ is the region in which the gas can be used as a fuel cell gas for power generation without carbon formation. In other words this region is the fuel gas region. In addition, the optimization of gas compositions...
Figure 7. Various hydrocarbons and related species in the C-H-O diagram.

Figure 8. Carbon deposition limit lines at various temperatures in the C-H-O diagram.
Figure 9. Electromotive force (theoretical open circuit voltage) in a fuel cell with air as an oxidant (a) at 1000°C and (b) at 600°C.
Figure 10. $H_2$ partial pressure (a) at 1000°C and (b) at 600°C.
is relevant to obtain a sufficiently high (open) cell voltage. Figure 9 is particularly useful since the theoretical open circuit voltage can be easily derived without any additional calculations once the C-H-O ratio is known.

Figure 9(b) shows the electromotive force of the same fuel cell (the concentration cell with air as an oxidant) at 600°C. As the extent of the carbon deposition region varies with decreasing temperature, the fuel gas region without carbon deposition shrinks toward the position of CO₂ on the oxygen-rich side but expands toward the position of CH₄ on the hydrogen-rich side. These data may be useful for intermediate-temperature fuel cells and for fuel cell reformers.

Figure 10 shows the partial pressure of H₂ ($p_{H₂}$) (a) at 1000°C and (b) at 600°C in the C-H-O diagrams. It can be found that these partial pressures are determined solely by the ratio of H and O within the carbon deposition region. Outside the carbon deposition region, $p_{H₂}$ decreases with increase in the content of H₂O, CO, and CO₂. In any way, since the equilibrium amounts (concentrations) are determined by the C-H-O ratio, the C-H-O diagrams are very useful to derive relevant information such as partial pressures of gaseous species. At the lower temperature (600°C), we can clearly find that $p_{H₂}$ within the carbon deposition region become much lower, so that the maximum of $p_{H₂}$ is ca. 0.7 bar. This temperature dependence arises from the fact that the partial pressure of CH₄ and CO₂ becomes nonnegligible, as the equilibrium reactions, C+2H₂ $\rightarrow$ CH₄, shift to the right side. Various other C-H-O diagrams are reported elsewhere (3).

CONCLUSIONS

Using thermochemical data of compounds consisting of carbon, hydrogen, and oxygen, the amounts of equilibrium products have been calculated for various fuel cell fuels including hydrocarbons, alcohols, as well as for other hydrocarbon-containing fuels such as biogas and coke oven gas. It has been shown that the equilibrium products from hydrocarbon-based fuel cell gases consist mainly of H₂(g), H₂O(g), CO(g), CO₂(g), CH₄(g), as well as solid graphite. For these possible fuel cell fuels, the minimum amounts of H₂O and O₂ needed for reforming are derived, in order to prevent carbon deposition. Equilibrium compositions are solely determined by the fraction of C, H, and O in the fuel gases. For a given C-H-O ratio, the equilibrium compositions are thus independent of the kinds of hydrocarboneous molecules.

The position for a given C-H-O ratio can be clearly presented in the C-H-O ternary diagrams. Such diagrams describing the carbon deposition region, the fuel gas region, partial pressures of various gases, and theoretical open circuit voltage have been successfully constructed. It has been pointed out that the C-H-O diagrams are very useful to derive such relevant operational conditions without any additional calculations, once the C-H-O ratio is specified.
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