



# Fuel processing for fuel cells and power to fuels as seen from an industrial perspective



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## ABSTRACT

Fuel cell and electrolysis depend critically on catalysis. Haldor Topsøe has been a leader in this field and initiated many innovations. The paper reviews the types of fuel cells, electrolyzers, and the thermodynamic aspects involved, and then discusses the technology from the viewpoint of available feedstocks. Important phenomena that determine the stability of the devices, such as carbon deposition and sulfur poisoning, are reviewed as well. Although fuel cells are still awaiting their commercial breakthrough, high-temperature electrolysis in combination with the catalytic synthesis undoubtedly has potential in sustainable energy scenarios.

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## 1. Introduction

Dr. Haldor Topsøe was keenly interested in fuel cell technology and followed the field closely. He supervised the many activities in Haldor Topsøe A/S related to fuel cells and in recognition of his efforts received the Grove medal in 2007 with the motivation:

“A unique contribution to the development of fuel cells throughout an extraordinarily long career”

The integration of solid oxide electrolyzers with the classical synthesis gas technologies also had his full attention.

The present paper will focus on the catalytic aspects related to fuel cell and electrolysis systems. This area is very wide and multidimensional because the optimum solution for the application of a fuel cell is a function of the type, the size of the installation and whether the application is stationary or mobile, and of course the nature of the fuel.

Recent reviews are available both for fuel processing for fuel cells and their catalytic aspects [1,2] as well as for solid oxide electrolyzer cells (SOEC) [3]. The present paper will mainly focus on the activities carried out in the Haldor Topsøe A/S company with emphasis on the industrial aspects.

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The paper is divided according to the fuel used as a feedstock for the different fuel cells, or the fuel that is actually produced by electrolysis, particularly by SOEC. Before addressing the fuel-specific aspects, we briefly discuss the different fuel cells and electrolyzers and sketch the thermodynamic framework. We also touch upon some pervasive challenges for the development of catalytic solutions for fuel cells and electrolyzers, namely carbon formation and sulfur poisoning.

## 2. Types of fuel cells and electrolyzers

Fuel cells and electrolyzers are classified according to the electrolyte used. Alkaline fuel cells (AFC) use hydroxide ions ( $\text{OH}^-$ ), which are normally supplied by using potassium hydroxide as the electrolyte. Nickel powder or Raney nickel is used as the anode. Operating temperatures range from 50 to 200 °C.

Proton exchange membrane fuel cells (PEMFC) use protons as charge carriers in the electrolyte, which is a solid polymer, most often sulphonated, perfluorinated polyethylene. Platinum is invariably used for the anode electrode. The PEMFC operates well already at room temperature but can be used up to around 100 °C.

In molten carbonate fuel cell (MCFC), carbonate ions ( $\text{CO}_3^{2-}$ ) in a lithium, sodium, or potassium carbonate melt are used as the

electrolyte. Nickel/chromium or nickel/aluminum alloys are used as anodes and operate around 650 °C.

Solid oxide fuel cells (SOFC) in their modern form use very thin (10 μm) oxygen ion-conducting ceramics as the electrolyte and thus inherently also function as an air separation device. The anode typically consists of nickel–ceramic (cermets) composites. The ceramic is most often yttrium-stabilized zirconia (YSZ). SOFCs have a wide window of operating temperatures, ranging from 550 to 1000 °C.

Low-temperature fuel cells, such as AFC, PEM, or phosphoric acid fuel cells (PAFC), can only use hydrogen as the fuel. The alkaline fuel cell (AFC) does not tolerate CO<sub>2</sub>, in the fuel or the air. PEM fuel cells can only handle limited amounts of CO (less than 100 ppm) and no ammonia. PAFC and high-temperature PEMFCs allow operation with a few percent of CO.

High-temperature cells such as MCFC and SOFC can use CO and CH<sub>4</sub> as a fuel directly, and ammonia is actually a perfect SOFC fuel. All fuel cells are sensitive to traces of sulfur, while carbon formation is an issue in the high-temperature fuel cells.

Alkaline and PEM fuel cells can be used in reverse mode as electrolyzers, and in fact, the alkaline electrolyzer has been in use for a century.

Solid oxide electrolysis (SOEC) has recently gained considerable attention owing to its high conversion efficiency, its ability to handle CO<sub>2</sub> or to perform co-electrolysis of steam, and CO<sub>2</sub> and is of great interest with regard to the impressive growth of intermittent power production from wind turbines and solar power. The ability to produce synthesis gas with any desired composition and the use of steam as feedstock open interesting opportunities for synergy with catalytic fuel synthesis.

### 3. Thermodynamics

The key benefit of fuel cell technology is the potential high electric efficiency, which is not limited by the Carnot efficiency such as mechanical power generators inevitably are [4,5].

The ideal electrical efficiency,  $\eta$ , of a fuel cell is

$$\eta = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S}{\Delta H} = 1 - T \frac{\Delta S}{\Delta H}$$

where  $\Delta G$  is the free energy change of the reaction, and  $\Delta H$  and  $\Delta S$  are the changes in enthalpy and entropy, respectively. Fig. 1 shows the plots of these efficiencies for some of the fuels discussed in this paper. It is evident that the efficiency for H<sub>2</sub> and CO used as a fuel drops at higher temperatures due to the positive entropy changes for the oxidation reaction. For methane, however, the efficiency is close to 100% and almost independent of temperature, as  $\Delta S$  is close to zero. For methanol fuel, the efficiency actually increases with temperature as  $\Delta S > 0$  and  $\Delta H < 0$  for the electrochemical oxidation

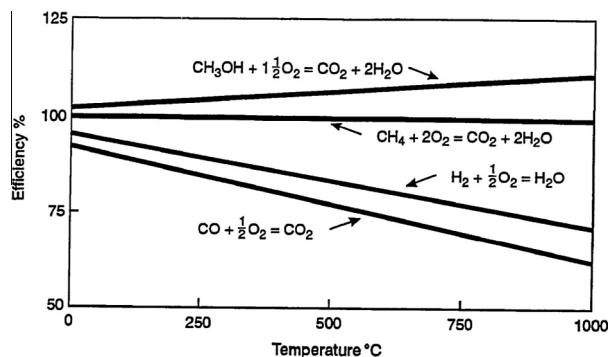


Fig. 1. Ideal electrical efficiencies for various fuels [5].

reaction. The theoretical efficiencies above 100% would require the supply of heat from an outside source.

These ideal efficiencies cannot be achieved in reality due to a number of loss mechanisms: activation overpotentials, ohmic losses, and mass transport or concentration losses. All of these irreversible losses generate heat, but some of it can actually be recuperated thanks to an important feature in high-temperature fuel cells: direct internal reforming in the anode chamber. Loosely speaking, the waste heat is utilized to drive the endothermal reforming reaction and thus upgrades the chemical energy content of the fuel. As the heat is supplied in situ in the anode, there is no temperature difference involved and thus no exergy loss accompanying the process.

The same synergy is present in SOEC electrolyzers where heat generated by loss mechanisms serves to split steam or CO<sub>2</sub>. In fact, high-temperature electrolyzers can operate with efficiencies,  $\eta_{\text{electrolyzer}}$  higher than 1, if external heat is available. This is because the minimum  $\Delta G$ , which must be supplied in the form of electricity, drops with temperature as illustrated in Fig. 2.

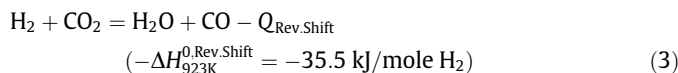
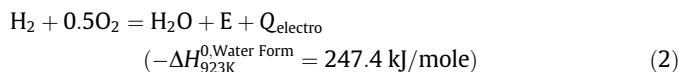
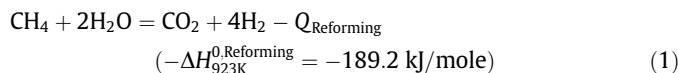
Normally, only the waste heat from electrolyzer cell imperfections is available. Conventionally, these are lumped into one area-specific resistance, called ASR. If the SOEC is then operated at a current density  $I_{\text{tn}}$ , where

$$\Delta H - \Delta G = \text{ASR} \cdot I_{\text{tn}}^2$$

the cell will operate in the thermoneutral mode, for example, there will be no temperature effects across the cell, which is very beneficial with respect to thermomechanical stresses on the ceramic/metallic components of the cell. The efficiency of the SOEC cell is then also close to 100% [6].

Finally, neither the fuel cells nor the electrolyzers operate with full conversion of the feed, as this would lead to low voltages and thus low efficiencies, due to a low Nernst potential. Furthermore, a too high utilization of fuel may lead to the destruction of nickel-based anodes due to oxidation to nickel oxide. For co-electrolysis, a too high CO<sub>2</sub> conversion can lead to carbon formation.

The principle of internal reforming can be utilized in high-temperature fuel cells (MCFC and SOFC) where the nickel anodes are catalytically active for the endothermal reaction in question. For methane, the nickel-based cermets in a SOFC have more than sufficient activity to equilibrate the steam-reforming reaction [2,7]. There are three interrelated reactions proceeding in the anode chamber:



where  $E$  is the electric energy produced,  $Q_{\text{electro}}$  is the electrochemically produced heat,  $Q_{\text{Reforming}}$  is the heat of the reforming reaction, and  $Q_{\text{Rev.Shift}}$  is the heat of the reverse shift reaction (the anode outlet temperature is normally higher than the anode inlet temperature). The reaction enthalpies are given at a typical operating temperature of 923 K. The quantities  $E$ ,  $Q_{\text{electro}}$ ,  $Q_{\text{Reforming}}$ , and  $Q_{\text{Rev.Shift}}$  are determined by:

$$-\Delta H_{923\text{K}}^{0,\text{Water}} = E + Q_{\text{electro}} \quad (4)$$

$$E = 2 \cdot F \cdot U \quad (5)$$

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