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Electric Power and Syngas from Methane—An Energy-Efficient Combination of a Single-Chamber Fuel Cell and Downstream Catalytic Equilibration

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The high-temperature solid oxide fuel cell (SOFC) is known for its stability and high efficiency. In contrast to many other fuel cells SOFCs not only tolerate but utilize even CO, such that the oxidation of H_2 as well as CO can be used to generate electric power. For this reason, in conventional SOCFs an upstream reformer usually converts methanol or hydrocarbons with water, CO_2, or O_2 to a mixture containing H_2 and CO for electrocatalytic oxidation. Problems in this approach include coking of the anode, resulting from the feed-gas separation required for the double-chamber configuration of conventional SOFCs, and the incomplete conversion in the reformer and the electrochemical oxidation. The selective oxidation of methane to CO and $2\,H_2$ (syngas) is exothermic with an enthalpy of about 36 kJ mol^{-1}. This heat of reaction is not enough for the efficient generation of thermal energy because the temperature gradients are too small, but it is high enough to result in potential hot-spot formation and to raise reactor safety issues. In addition, the thermodynamic driving force requires temperatures above 800 °C for the selective formation of syngas. The partial oxidation of methane (POM) and oxygen to syngas has been the subject of intensive studies during the last 10 years. Typical catalysts are based on nickel and cobalt, where the former tends to coking and the latter tends to deactivation.[1] There are many approaches to improve the catalytic properties by doping, especially with rare-earth elements.[1]

Research groups from China, Australia, and Korea have used a different approach; they collected electric power from the electrocatalytic conversion of CH_4 and O_2 (2:1) to a mixture of H_2O, CO, H_2, CH_4, CO_2, and O_2.[2] The electrochemical partial oxidation (EPOX) is carried out in a single-chamber SOFC (SC-SOFC) and proceeds without coking. The complex product-gas mixture is passed downstream over a syngas catalyst, which drives the mixture towards its thermodynamic equilibrium, nearly pure CO and H_2 (1:2) with release of heat [Eq. (1)]. The thus-produced syngas could then be converted further as desired. The charm of the new method in contrast to the direct conversion of CH_4 and O_2 to syngas (POM) at high temperatures is the generation of electric power and the increased reactor safety because of reduced exothermicity.

$$\begin{array}{cccccccc} & & & CO & & & & \\ & & & CO_2 & & & & \\ 2\,CH_4 + O_2 \rightarrow & \text{fuel cell} & \rightarrow & CH_4 & \rightarrow & \text{catalyst} \rightarrow & CO + 2\,H_2 & \\ & \downarrow & & H_2O & & \downarrow & \downarrow & \\ & \text{electric power} & & O_2 & & \multicolumn{2}{c}{\text{thermal energy}} & \end{array} \tag{1}$$

What is so special about this new approach? In conventional dual-chamber SOFCs the two electrode compartments are separated by an oxygen-conducting ceramic (electric insulator) and individually supplied with methane (anode) and oxygen (cathode) to produce electric power and CO_2 and H_2O. Especially on the anode, because of the high temperature, there is also a thermodynamic CO formation resulting in coking due to the Boudouard reaction. Coking at the Ni anode results in high activation polarization and a rapid decrease of the electric cell performance. Interestingly an oxygen concentration of only a few percent on the anode side is sufficient to prevent coking.[3] Another problem is the high working temperature of the SOFC, which requires high standards for the compartment sealings. In a SC-SOFC the feed gases are mixed upstream and flow across both electrodes, so no seals are required. Owing to the high oxygen content in the feed gas and the formation of water, anode coking does not occur.[4] Catalytic oxidation reactions apparently prevent the formation of carbon layers and carbon fibers at these high temperatures. Hibino et al. have demonstrated the advantages of SC-SOFCs with the selective electrocatalytic oxidation of methane, ethane, and propane at 350–500 °C (no noble metals, no catalyst poisoning by CO, no evidence of coking, low cost).[5] The remarkable development of the SC-SOFC from the beginning in 1999 to today is documented by electric power production comparable to that of traditional dual-chamber SOFCs.[4]

Of critical importance for SOFC applications is the selection of materials for the electrodes and the electrolyte. This holds especially for the SC-SOFC, in which both electrodes face the same feed gas mixture. For the selective oxidation of methane at the anode this requires effective

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methane activation at the electrode surface despite the presence of gaseous oxygen in high concentrations, while at the cathode oxygen must be activated in the presence of excess methane. This means there should be no competitive adsorption of oxygen on the anode, while on the cathode methane should not compete with oxygen activation. These requirements are apparently matched by the SC-SOFC presented by Shao et al.[2]

The SC-SOFC is based on a Ni/YSZ-cermet supported fuel cell (cermet:composite composed of ceramic and metallic materials). Yttrium-stabilized zirconium oxide (YSZ) with 8 mol % YO_2 is the most commonly used anode material in SOFC applications. Among the drawbacks of YSZ as a solid-state ion conductor are its high working temperature, which prevents applications below 650 °C, and the lack of catalytic activity. Here nickel comes into the game; it is accessible, has a high temperature stability, and provides excellent electrocatalytic activities for H_2, CO, and hydrocarbon oxidation. Among the drawbacks are its tendency to promote coking and a high thermal expansion coefficient compared to that of YSZ. The best solution so far is the formation of a Ni-YSC composite (Ni-cermet), whose thermal expansion coefficient matches that of pure YSZ. Furthermore, such correctly prepared Ni-cermet anodes show a significantly less undesired electrode polarization than anodes of pure nickel. Therefore porous Ni-YSC layers presently represent the most successful low-cost anode material for SOFC applications.[6]

The cathode in this type of cell activates and reduces oxygen and conducts it as oxygen ions. Cerium oxide has long been known as an excellent catalyst for methane oxidation, but it is a very poor ion conductor. Doping with Gd, Sm, or Y results in up to tenfold improvement of the ion conductivity over that of YSZ at medium temperatures of 500–800 °C with Sm (samarium-doped cerium oxide SDC) as the most promising dopant in an oxidizing atmosphere.[7]

SDC is now being used increasingly as an electrolyte in SOFCs for medium-temperature applications. In early Ce-based SC-SOFCs one disadvantage was the reduced open-circuit voltage resulting from the electric conductivity of Ce-based ionic conductors at increasing temperatures.[8] A key property of the cathode in a SC-SOFC is its high activity for oxygen reduction in combination with a strongly reduced activity for fuel oxidation in an oxygen-rich environment, that is, selective activation of oxygen in the presence of excess methane. Because of its good catalytic activities for oxidation reactions at increased temperatures, pure SDC is not a suitable cathode material for the SC-SOFC. Among other promising materials the perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) displays the desired properties. In fuel-cell applications the physical mixture of BSCF with SDC tempered at 1000 °C has led to promising results.[9] Such BSCF-SDC cathodes show lower activities than SCC for the electrocatalytic oxidation of propane ($Sm_{0.5}Sr_{0.5}CoO_3$) and LSCF ($La_{0.8}Ssr_{0.2}Co_{0.2}Fe_{0.8}O_3$).[10] BSCF-SDC exhibits already at 650 °C excellent electrocatalytic activities for oxygen reduction, which makes it a promising cathode material for the SOFC at medium temperatures.[11]

The SC-SOFC with downstream isomerization reported by Shao et al. has the follwing composition (see Figure 1): a BSCF/SDC (7:3) layer (thickness 20 μm) on a 5 μm thick SDC layer functions as the cathode; this is separated from the Ni/YSZ-cermet (6:4, 700 μm) anode by an at least 5 μm thick YSZ layer. Through the separation of the BSCF-SDC layer from the YSZ layer and the SDC layer from the Ni-cermet, solid-state interface reactions are avoided, which are known to result in the formation of isolating regions. The undesired electric conductivity of SDC at higher temperatures is apparently blocked successfully by the YSZ layer, as documented by an open-circuit voltage of 1.05 V. Remarkable are the reported power densities of over 1500 mW cm^{-2}, which represents a significant improvement over the previously reported power densities of up to 700 mW cm^{-2} for propane oxidation on SC-SOFC.[4]

In Figure 2 the cell voltage and cell performance of the SC-SOFC ($CH_4/O_2 = 2{:}1$ at cathode and anode) are compared with those of a DC-SOFC (cathode: $CH_4/O_2 = 2{:}1$, anode: air); the two fuel cells were composed of the same materials. Here, the SC-SOFC shows better performance. Owing to its limited activity for POM at temperatures below 850 °C, the methane conversion at the BSCF-SCD cathode remains below 50 % with H_2, CO, CO_2, and H_2O as products. At temperatures of 600–850 °C downstream product equilibration with a Gd-doped Ni/Al_2O_3-catalyst results in a methane conversion of > 95 % with selective syngas formation ($CO/H_2 = 1{:}2$).[2] Unfortunately, besides its composition (5.6 wt % Gd_2O_3, 15 wt % Ni on Al_2O_3)[2] very little has been reported on this Gd/Ni catalyst. In one publication Branco et al. report high activity and no tendency to coking for Gd-Ni and Lu-Ni

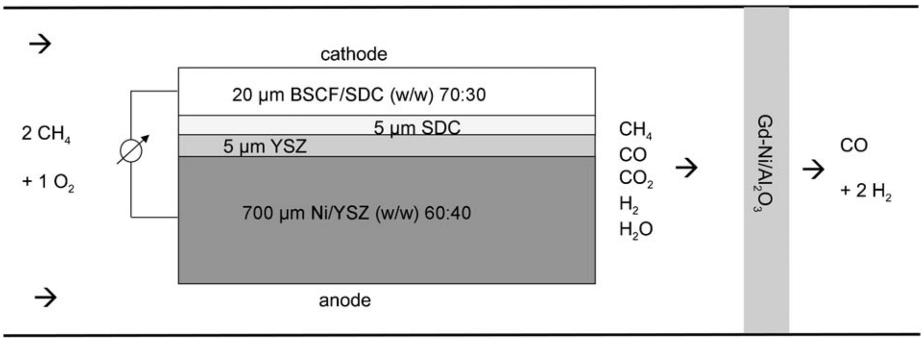

Figure 1. Construction of the SC-SOFC reactor with downstream isomerization of the product gas mixture.[2]

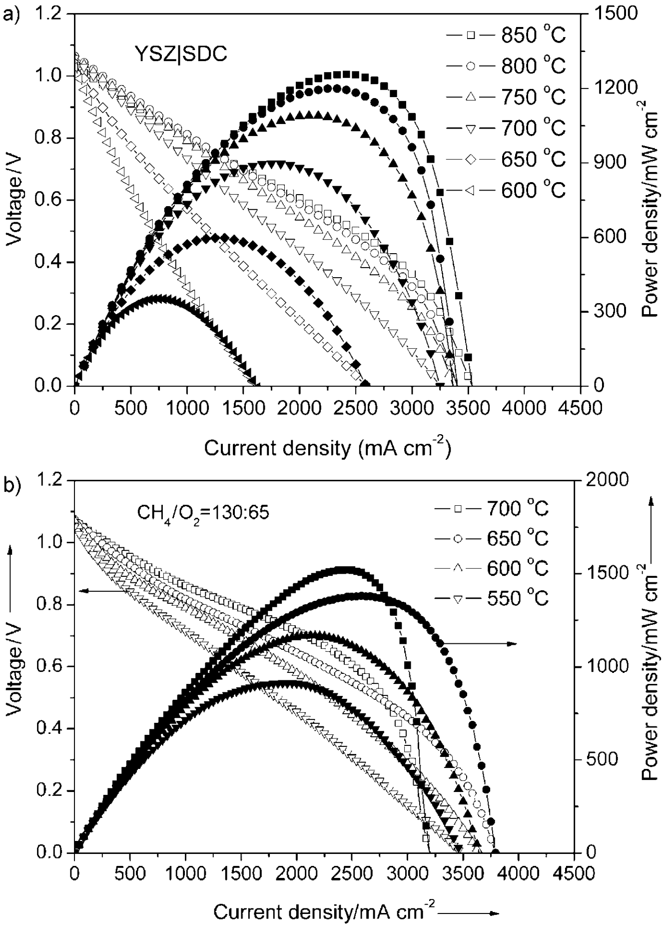

Figure 2. Comparison of the temperature-dependent power production of the SOFC for POM in the conventional dual-chamber configuration (a) with that in the single-chamber configuration (b).[2]

catalysts in their POM studies.[12] It can be assumed that any other POM catalysts with a low tendency to coking could be used alternatively.

The upper explosion limit of methane lies at < 20 vol %,[4] but the SOFC can be operated safely with an undiluted mixture of 66 vol% CH_4 and 33 vol% $O_2 = 2:1$, which is beneficial for power production. The SOFC produces electric power through the partial equilibration of the POM reaction, which utilizes with high efficiency a significant portion of the thermal energy. Potential safety hazards through explosions or runaway conditions in the downstream operation are thus reduced significantly. Beneficial for ion conductivity and catalytic activity in continuous operation is an increased temperature of 100–150 °C of the fuel cell relative to the oven temperature due to the catalytic reaction. The final product gas is produced at a high temperature and can be cooled efficiently with production of thermal energy to the reaction temperatures of 200–300 °C needed for methanol or Fischer–Tropsch synthesis. Since the syngas has already close to optimal composition only pressurization to 20–50 bar is needed for further processing, which presents no technical problem at these temperatures.

If this combination of SC-SOFC with downstream equilibration developed by Shao et al.[2] is approved in practical industrial applications, the single-chamber fuel cell may have a bright future because of its simplified construction and ease of operation. Additional advantages are that it is free of noble metals, has no propensity for coking, and is stable to CO. Biogas, natural gas, and higher hydrocarbons may now be converted to methanol or hydrocarbon mixtures (Fischer–Tropsch) with more efficient production of electric power and thermal energy. Potential for further fine-tuning of the electrodes and electrolytes remain.

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