# A1512

# Hydrogen and syngas production by solid oxide electrolysis with solar heat integration

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## Abstract

Solid oxide electrolysis is especially attractive in terms of efficiency if coupled with a high temperature heat source. The external thermal energy can be used to evaporate the supplied process water and to heat up the steam and/or the carbon dioxide to the required electrolysis temperature. The external heat is ideally generated by renewable and environmental-friendly sources, such as solar radiation. The main challenges in this approach is the coupling between an intermittent heat source and the solid oxide electrolyser stack and its operation with environmental varying conditions while enabling high efficiency and low degradation.

Here we report the recent results of the project "Future Fuels 2" at the German Aerospace Center (DLR). The aim is to investigate the production of green hydrogen and syngas by means of solar heat integrated solid oxide electrolysis. In this project a test platform for syngas production was developed at DLR, consisting of a solar thermal steam generator and 12-cells stack, which was supplied by SOLIDpower S.p.A (Mezzolombardo, Italy). The solar heat was supplied by a high flux solar simulator based on elliptical reflectors with 10 xenon short-arc lamps. The test platform optimizations, e.g. reduction of the heat losses, minimization of steam instabilities and increase of the steam temperature, are outlined.

Results on the stack behavior in steam and co-electrolysis are presented and discussed. The stack was operated for 200 h in co-electrolysis mode under intermittent supply of steam, and $CO_2$, powered with solar heat and of electrical power, respectively. These varying operating conditions simulate fluctuations of the renewable energies, e.g. high solar radiation, clouds formation and day-night cycle. Both, in steam- and in co-electrolysis the SOEC stack showed a very good and homogeneous behavior at 750°C and 90 % gas conversion. In order to convert 90 % of the supplied process gases, which corresponds to 7.5 slpm of produced $H_2$ or $CO+H_2$ syngas, an electrolysis power of ca. -1.5 kW was necessary. High electrical efficiencies of 89% (steam electrolysis) and 93 % (co-electrolysis) were achieved. The stack behaviour in both electrolysis modes was almost identical. During the intermittent operation altogether 14 000 liters of syngas ($H_2+CO$) were produced successfully. Moreover, the stack degradation was very low.

# Introduction

The efficiency of solid oxide electrolysis (SOE) can be significantly increased by providing high temperature thermal energy from external sources [1]. From the thermodynamic point of view, part of the required entropic heat demand for the endothermic decomposition of steam and/or carbon dioxide can be provided by high temperature heat from solar thermal power or waste heat from industrial processes. This results in a significant reduction of the required electricity demand for the electrolysis [2] resulting in low costs of the produced $H_2$ and/or syngas.

# 1. Scientific Approach

The aim of the project "Future Fuels 2" at the German Aerospace Center (DLR) is to investigate the production of green hydrogen and syngas by means of solar heat integrated solid oxide electrolysis. In this project a test platform for $H_2$ and syngas production was developed consisting in 12-cells stack (SOLIDpower S.p.A, Mezzolombardo, Italy) and a solar thermal steam generator (DLR). The solar heat was supplied by a high flux solar simulator based on elliptical reflectors with 10 xenon short-arc lamps to a solar steam generator. In the Future Fuels 2 project the solar heat was applied to evaporate and heat the supplied electrolysis water. The objective was to super-heat the produced steam up to the required temperature level of the SOEC electrolyzer, thus reaching high electrical stack efficiency. On-going and further activities (e.g. "NeoFuels" project) aim to further increase the efficiency of the SOE electrolysis by applying solar thermal energy not only to the water but also to the other input process gases ($CO_2$ and air).

# 2. Experiments

Figure 1 shows the experimental setup of the solar heated solid oxide electrolyzer test platform for $H_2$ and syngas production. This laboratory prototype system consists of 5 main components: 1) solar simulator, 2) solar steam generator, 3) water supply system, 4) solid oxide electrolyzer and 5) control unit. Auxiliary components of the system are flow meters and valves to control the mass flows and the pressures of the process media, e.g. water, steam, $H_2$ $CO_2$ and air, several temperature and pressure sensors and controllers, peripheral electrical tube heaters, mass flow controllers for the fuel gas and air, DC voltage power supply, electronic load and data acquisition system.

Highly purified water was fed to the steam generator, which contains a conical spiral tube for the heat transfer. Concentrated solar radiation incident on the receiver cavity was absorbed by the spiral tube, which evaporates and heats the water to high temperature steam. The solar radiation was generated by a high flux solar simulator, which consists of 10 xenon short-arc lamps with elliptical reflectors with a maximal overall solar radiation power of 20 kW. For the steam generation of this project only two xenon lamps were used. An important issue was the increase of the temperature of the steam in the solar steam generator up to the required temperature of the electrolyzer. More details of this task are described below (see Figure 3).

The superheated steam with a flow rate of 2.5 kg/h was supplied to the SOEC electrolyzer via thermally isolated tubes. Since the 12-cell laboratory scale SOEC electrolyzer stack

could not process steam mass flows higher than 0.5 kg/h a large fraction of the steam had to be bypassed to the environment. The system pressure and the mass flow of steam to the electrolyzer were controlled by the relative setting of two valves placed in the bypass line (steam vented to environment) and in the line to the electrolyzer. An important challenge was the minimization of the pressure fluctuations of the steam entering the SOEC stack. This issue was solved by properly adjustment of the water flow rate, the solar radiation and the pressure drop in the steam generator to each other. Moreover, in order to increase the overall efficiency of the test platform the heat losses of the superheated steam had to be minimized. Therefore, the solar steam generator and the SOEC electrolyzer were located as close as possible to each other. Additionally, the thermal insulation of the tubes for the transfer of the superheated steam from the steam generator to the SOEC electrolyzer were optimized.

By supplying electrical power to the SOEC stack, the superheated steam was decomposed into $H_2$ and $O_2$. The electrical current was controlled by an electronic load. For generating $CO+H_2$ syngas, additional $CO_2$ was fed from the control unit to the stack. Gas coolers were used to cool down both process gases to room temperature. All system components were controlled remotely by industrial programmable logic controllers ("Siemens Simatic S7"). This ensured safe and reliable operation. In order to monitor possible system instabilities a fast data sampling rate of 1 s was selected. More details of the test platform components can be taken from [3].
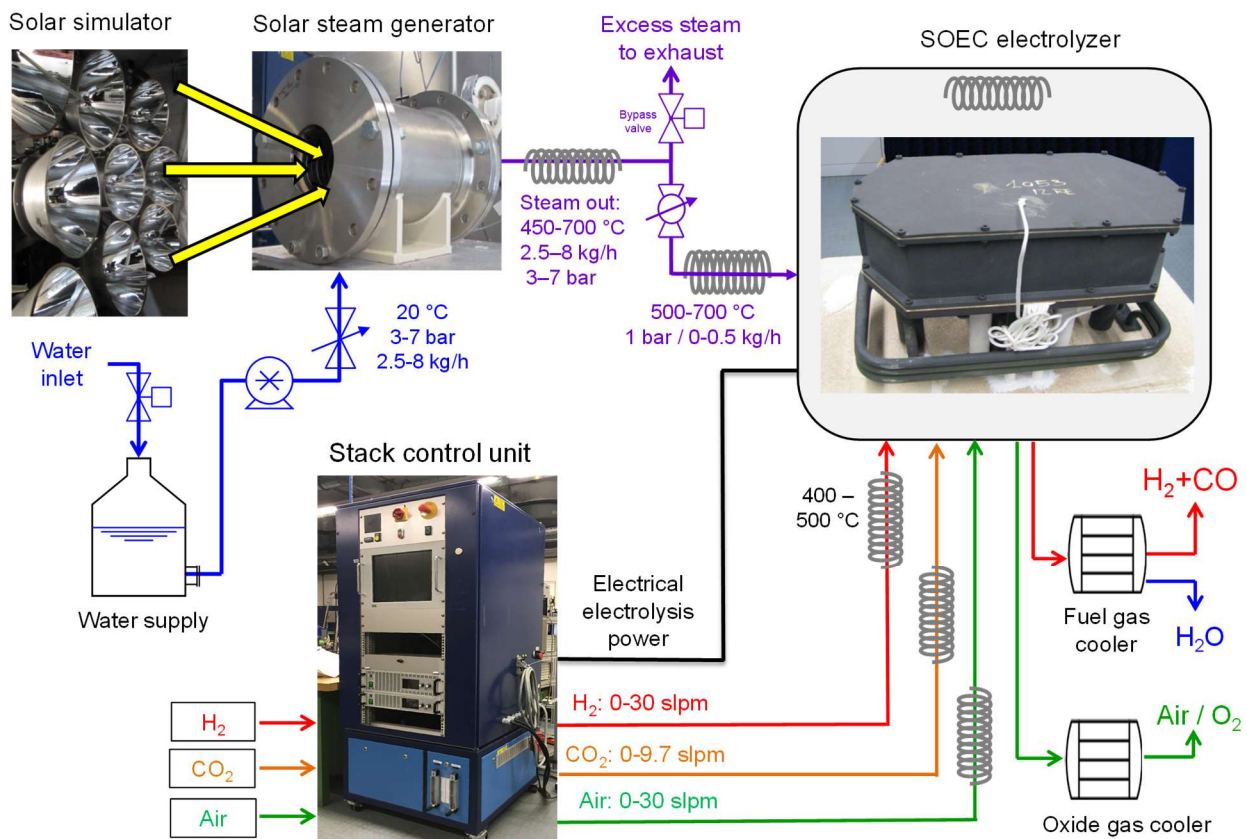


Figure 1: Laboratory prototype of solar heated solid oxide electrolyzer test platform for $H_2$ and syngas production

A photograph of the solar heated solid oxide electrolyzer test platform in operation is shown in Figure 2.

Figure 2: Solar heated solid oxide electrolyzer test platform in operation

The SOEC stack consisted of 12 repeat unit (RU) with ASC cells, each with an active area of 80 cm$^2$. In order to analyze the stack homogeneity, each RU was fitted with a separate voltage probe. The stack temperature was measured with a thermocouple located below the stack. The stack was characterized mainly by current-voltage measurement and gas analysis. Moreover, the stack was operated for 200 h in steam- and co-electrolysis mode under intermittent supply of steam, of $CO_2$, of solar heat and of electrical power in order to simulate fluctuation of the renewable energies (high solar radiation, clouds, day-night cycles). All measurements were recorded according to pre-normative test procedures [4].

# 3. Results

**Solar steam generation**

Figure 3 shows the cross section of the spiral solar receiver (solar steam generator) in operation with the measured temperatures near the conical spiral tube. The tube is 10 mm in diameter and 1.5 mm in thickness and was made from high temperature stainless steel (1.4841). The further construction details of the receiver are presented in [3]. The steam receiver operation parameters were optimized during the intermittent test operations. Therefore, the water flow rate was set to 2.5 kg/h throughout the test and the receiver was irradiated with only two lamps with a total power of 3.7 kW. This reduced the excess steam flowing through the bypass valve (see Figure 1) and hence minimized energy losses.

The temperature of the water/steam inside the steam generator increases from ca. 120 °C at the solar radiation inlet to more than 700°C at the outlet from the steam generator. Hence, by adjusting the intensity of the solar radiation and the water flow rate, the steam temperatures can be controlled to the required temperature of the SOEC electrolysis process. The input of this renewable heat enables to operate the SOEC electrolyzer with intermittent or variable part-load conditions with high electrical efficiency.
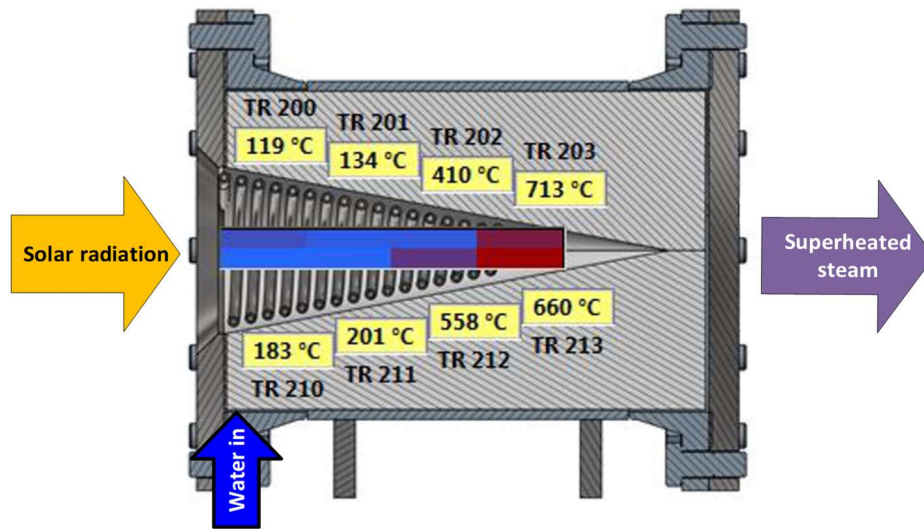
Figure 3: Cross section of the solar steam generation in operation

## H$_2$ and syngas production by solar heat integrated electrolysis

Figure 6 shows the current-voltage behavior and the temperature of the SOEC stack in steam and co-electrolysis with increasing and decreasing current density. In steam electrolysis the stack was operated at 753°C (OCV) and supplied with 8.28 slpm of steam, which was delivered from the solar steam generator. In co-electrolysis at 750°C (OCV) the stack was supplied with 4.14 slpm steam and 4.14 slpm CO$_2$. In order to prevent reoxidation of the ASC cells in both cases 10% of H$_2$ was added. The stack was operated for 1 h at the highest current density, which corresponds to 90% conversion, in order to reach thermal equilibrium.
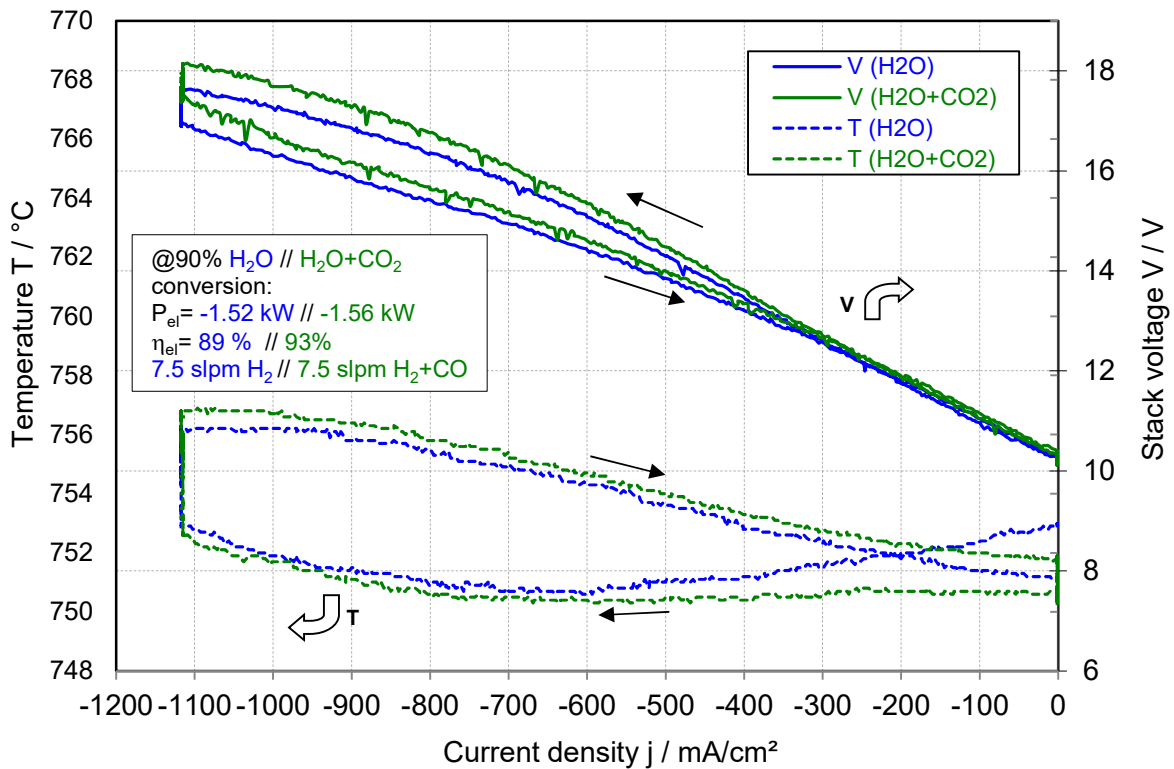


Figure 4: Current-voltage behavior and temperature of the SOEC stack in steam- and co-electrolysis

The open circuit voltage (OCV) of the stack in both cases was ca. 10.3 V which is in good agreement with the theoretical value calculated with the Nernst equation. This indicates good gas tightness and high quality of the stack sealing. The stack voltages increased almost linearly with increasing current density. This behavior is well-known for SOEC and can be attributed to low activation polarization resistances of the fuel and oxygen electrodes [5]. The observed hysteresis between the upward and backward curves is a result of not reaching thermal equilibrium. This issue will be discussed below. However, the stack voltage instabilities were almost neglectable, which is due to the successful above-mentioned minimization of the pressure drop fluctuations in the steam generator.

At a current density of -1120 Acm$^{-2}$ the voltage in steam electrolysis was approximately 17.0 V, which resulted in an electrolysis power of -1.52 kW. At this operation conditions a steam conversion rate of 90% was achieved which corresponds to a production of 7.5 slpm of hydrogen. This results in a high electrical stack efficiency of 89 % depending on the lower heating value (LHV) of $H_2$. Even at this high steam conversion the average electrolysis voltage per RU of 1.4 V was below the maximum voltage limit of 1.6 V given by the stack manufacturer. Hence, even higher steam conversion rates might be feasible. Moreover, in both modes the stack showed a rather good homogeneity across its height. The electrolysis voltages of the RUs, except RU 1 at the bottom and RU 12 at the top, of ca. 1.4 V at 90% steam conversion were almost the same. The higher voltages of the RUs at the bottom and top of 1.6 V can either be explained by higher contact resistances and/or lower temperatures.

In co-electrolysis a voltage of 17.5 V at a current density of -1120 mAcm$^{-2}$ was required in order to convert 90 % of the supplied process gases. This corresponded to a stack power of ca. -1.56 kW, an electrical stack efficiency of 93 % and 7.5 SLPM of produced syngas. The higher electrical stack efficiency in co-electrolysis is due to the higher LHV of CO compared to $H_2$. Similar to steam electrolysis the voltages of the top and bottom RUs are ca. 0.2 V higher compared to the others, which are in the range 1.40 V – 1.45 V. These initial SOEC performance data are very good in comparison to previously reported stack performance values [6-13].

The temperatures of both curves revealed hysteresis behavior, which is a result of the thermal inertia of the stack. Especially for steam electrolysis the stack temperature decreased with increasing current density due to the endothermic decomposition reaction of $H_2O$. For co-electrolysis the effect is less pronounced. However, in both cases the temperatures increased for current densities higher than -650 mA/cm$^2$. During galvanostatic operation for 1 h at the highest current density the temperatures raised by 3-4 K to 757°C. The corresponding average electrolysis voltages of the RUs (excluding bottom and top) at these operating conditions are 1.36 V for steam electrolysis and 1.42 V for co-electrolysis. The theoretical thermo-neutral voltages (TNV) at 750°C for steam and pure $CO_2$-electrolysis are 1.285 V and 1.462 V. The TNV for co-electrolysis of a 50%$H_2O$+50%$CO_2$ mixture is in between these two values. Since the measured electrolysis voltages are in the range or even higher compared to the theoretical TNVs, the stack has already reached exothermic mode at 90% gas conversion, thus producing thermal energy.

**Intermittent operation of SOE platform**

Figure 5 shows the behavior of the SOEC stack during 200 h of intermittent operation. The test can be separated in 5 different operation categories, which are:

1)     start-up and shut-down of the system
2)     standby operation at 750°C and OCV with cloud formation at daytime
3)     electrolysis operation at 750°C with solar radiation at daytime,
4)     standby operation at 630°C without solar radiation during night
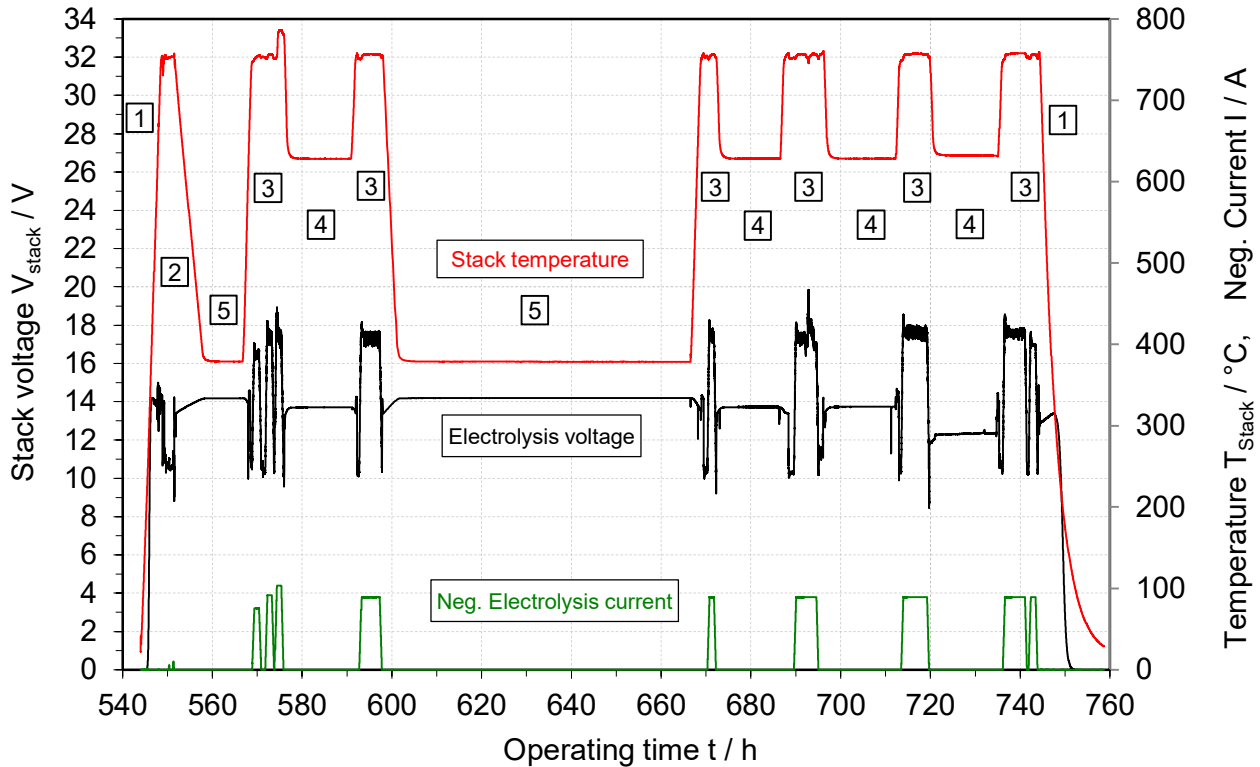5)     standby operation at 380°C without of solar radiation for several days.



Figure 5: Intermittent operation of the SOEC stack mainly in
co-electrolysis with solar heat integration during 200 h

During the 200 h of intermittent test of the system, the stack was operated in total for 30 h mainly in co-electrolysis mode with solar heat integration. During this time altogether 14000 liters of $CO+H_2$ syngas were produced at 90% gas conversion with overall stack efficiency of 93%. The production of CO in the syngas was proven with gas analysis. During the intermittent operation the stack showed a stable and homogeneous behavior with low degradation.

# Acknowledgement

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