Integrated System Design of a Small-scale Power-to-Methane Demonstrator

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Power-to-methane technology has been considered as a promising alternative to cope with seasonal storage of renewable energy and the utilization of CO_2 captured from various sources, due to the existing infrastructure for massive methane storage and distribution. The performance of a power-to-methane system is almost defined by the type and the design point of the electrolyzer. The inherent high electrical efficiency of solid oxide electrolyzer makes it rather promising for a highly efficient power-to-methane system. However, the large amount of heat needed for steam generation limits the overall efficiency of a standalone electrolyzer. Fortunately, the strong exothermic methanation reaction offers a good opportunity for heat integration, thus possibly increasing the overall HHV efficiency above 85 %. Regarding to this context, a power-to-methane test rig based on a full stack of solid oxide electrolyzer is currently under design and demonstration.

In this paper, the critical issues related to the design of such an integrated system are addressed: (1) selecting the nominal operating point of the electrolyzer to minimize electrical heating at no cost of efficiency and (2) maximizing the benefit from the system integration at no cost of operation flexibility. A quasi 2D model of the electrolyzer considering detailed mass transport across the electrodes has been developed and calibrated to understand the electrolyzer performance that is not revealed by experiments. Then, the system design is investigated by varying the utilization factor and the cell temperature. The most promising practical design point with an overall efficiency around 85 % and no electrical heating is selected with the design of a specific heat exchanger network to maximize the heat integration with a minimum number of connections between the electrolyzer and the methanation subsystems.

1. Introduction

Energy storage for bulk power management has been one key issue to address the increasing penetration and massive use of renewable energies, e.g., solar and wind power, due to the frequent mismatch of available renewable energy sources and energy demand. Among the available technologies for energy storage, only pumped-hydro, compressed-air and thermal energy storage are suitable for long-time storage. However, these technologies suffer from either strict geographical constraint, high capital investment, or low round-trip efficiency. Thus, converting renewable energies, whenever available, to easy-to-store/transport chemicals via power-to-gas/liquid technologies (PtG/PtL) has been considered as a promising choice for massive energy storage (CHBC, 2017) and is currently under intensive research, development and demonstration. Particularly, power-to-methane (PtM) technology has been further highlighted due to the available storage infrastructure.

The core component of PtG is the electrolyzer, which uses electrical power to electrochemically split water to H_2/O_2 and prevents the H_2/O_2 remixing by a selective membrane/electrolyte. Available electrolysis technologies include commercially-available low-temperature (40 - 100 ºC) water electrolysis with an alkaline or acidic electrolyte, and laboratory/commercially-ready high-temperature (650 - 850 ºC) steam electrolysis (HTEL) with a solid-oxide electrolyte (SOE). The HTEL operates below 1.4 V cell voltage with a current density between 0.4 - 0.8 A/cm^2, thus offering much higher electrical efficiency and round-trip efficiency. Particularly, the high operating temperature offers the opportunity for heat and power cogeneration, thus

ensuring a high overall system efficiency. The HTEL cost is expected to be reduced significantly in the future by continuous R&D and massive production, thus further improving its competitiveness. A big challenge for practical HTEL system design is to efficiently and reliably heat the fed water and sweep gas to desired temperature (650 - 750 ºC). This is not an easy task, as (1) the amount of heat is large due to steam generation; and (2) the final temperature required is rather high. In most experiment setups, this task is achieved by electrical heating. However, the practical experience shows that the electrical heating is not reliable and fails frequently. Thus, in practice, the electrical heating may only be used for start-up or fluctuation regulation, and should be avoided during continuous operation.

Therefore, in this paper, we cope with the system design and feasibility evaluation of a small-scale, atmospheric, HTEL-based, power-to-methane demonstration. The initial target of the system design described in this paper is to minimize electrical heating during normal operation. To achieve this, heat integration should be emphasized to maximize the heat utilization of the whole system, as the highly-exothermic methanation reaction of CO_2 and H_2 can supply substantial amount of heat for steam generation.
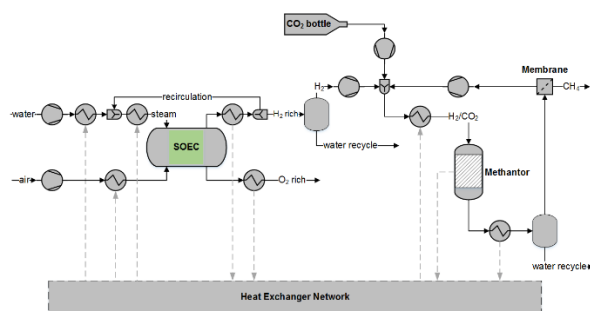

Figure 1: The flowsheet of the power-to-methane demonstrator (components for start-up, hot stand-by and temporary storage not included)

2. Description of the power-to-methane demonstrator

The demonstrator is based on Solid Oxide Electrolyte Cell (SOEC) and catalytic methanation to pursue better dynamic response. The component sizing is defined by the SOEC hardware, and its nominal operating mode and conditions. The current plan is to comprise one full stack with 64 cells (80 cm^2 per cell) operating under atmospheric pressure. The total power consumption ranges from 3 to 6 kW, depending on the operating mode and conditions of SOEC. The provisional initial flowsheet of the SOEC-based demonstrator, as illustrated in Figure 1, employs one-stage catalytic, fixed-bed methanation reactor: Water is pumped first pre-treated and vaporized. The steam is then mixed with cold H_2-rich recirculation to keep around 10 % of H_2 presented in the fuel feed flow, so that the fuel electrode is under reduced condition ensuring good catalyst activity. The H_2/steam mixture is then superheated to around 700 ºC and enters the SOEC stack, where the fed steam is split into H_2 and O^{2-} at the fuel side (hydrogen evolution reaction, HER), while the O^{2-} ion is transported across the electrolyte to the oxygen evolution reaction (OER) side. To remove the O_2 generated, sweep air heated up to the same temperature as the HER feed is fed to OER. Ideally, all H_2O fed at HER can be split; however, due to the limitation of, e.g., mass transport of molecules across electrodes, currently only up to 90 % of the fed steam can be split. Thus, the H_2-rich mixture out of the SOEC stack is first cooled down and H_2O is then removed in a subsequent flash drum. The purity of the saturated H_2 out of the flash vessel depends on the operating pressure and cooling temperature. The higher the pressure and, the lower the temperature, the higher H_2 purity can be simply obtained. The dry H_2 is compressed, mixed with CO_2, and pre-heated up to around 230 ºC before entering methanation reactor. The outgoing gas mixture of the reactor is cooled, and the contented water is separated and may be recycled. As a membrane is employed to upgrade the CH_4, the ratio of H_2/CO_2 should be slightly deviated from the stoichiometry ratio of H_2/CO_2 reaction (i.e., 4) so that either CO_2 or H_2 is completely converted. In practice, an over-supply of H_2 will be used to avoid coke formation on the catalyst, which is promoted in the presence of CO_2 alone. The membrane for upgrading CH_4 from a CH_4/H_2 or CH_4/CO_2 mixture has been commercially available. The unreacted gas is compressed and mixed with H_2 and CO_2 feed streams. The molar purity of CH_4 product is expected to be beyond 96 %.

3. Component modelling

3.1 Solid Oxide Electrolyte Cell

A quasi 2D model adapted from (Menon, 2015) is implemented in Aspen Custom Modeller (version 8.8), and calibrated by parameter estimation based on the available experimental data (Kotisaari2016; Bernadet, 2015):

(a) short-stack (6 cells) test under atmospheric pressure and at three different temperatures (700, 750 and 800 ºC) with a fuel (H_2/H_2O = 1/9)/air flowrate of 12/51.4 normal millilitre per minute per cm^2 (NmLPM/cm^2), and (b) single-cell (3.14 cm^2) test under 10 bar and at 800 ºC with a fuel feed ($H_2O/H_2/N_2$ = 58.5/6.5/35) flowrate of 18.46 NmLPM/cm^2.The predictions based on the calibrated model agree quite well with all experimental data employed (Figure 2). Particularly, the substantial increase in operating voltage of the atmospheric test in Figure 2b due to the mass transport limitation (fuel shortage) is successfully captured. Therefore, the model is expected to accurately predict the performance of a full stack at various conditions.

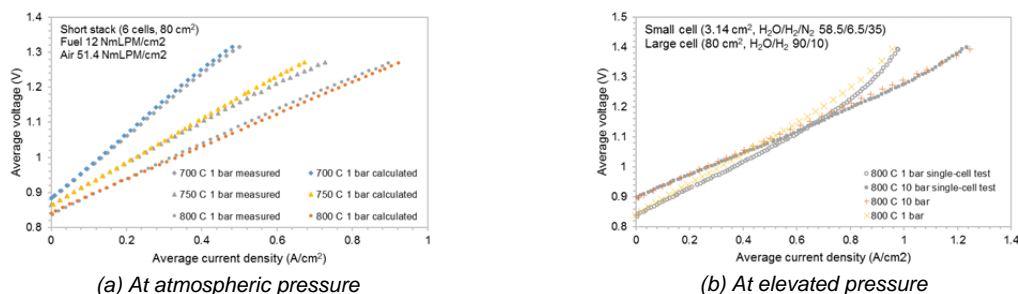*(a) At atmospheric pressure*   *(b) At elevated pressure*

Figure 2: Comparison of model prediction and experiment results for solid oxide electrolyzer (The experimental data are provided by EU FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621173, SOPHIA, and reported in Bernadet (2015) and also in (Kotisaari(2016).
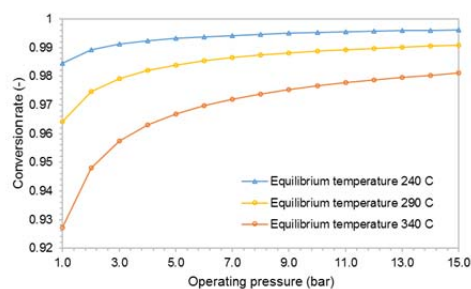

Figure 3: Conversion rate versus reacting temperature and pressure for CO_2 methanation reaction

3.2 Isothermal catalytic methanation reactor

The methanation reaction of CO_2 and H_2 is equilibrium limited and highly-exothermic. The single-pass conversion rate of the reactants is highly affected by the reacting pressure, temperature and the activity of the employed catalyst. The thermodynamic analysis of the reaction equilibrium at different operating conditions (Figure 3) illustrates that a higher pressure and a lower temperature are preferred of such exothermic reaction. The lower the temperature, the smaller the effect of pressure on conversion rate will be. At an equilibrium temperature of 340 ºC, the benefit of pressure increase is limited after 10 bar; while it is around only 3 bar for a temperature of 240 ºC. However, for catalytic reaction, the temperature cannot be too low regarding to the catalyst activity. A screening of Ni-based catalysts, including composite oxide supported catalysts, hydrotalcite-derived Ni/Al_2O_3 and several commercial catalysts, has been performed in HELMETH project (Founti, 2016), which illustrates that the operating temperature within the range from 275 to 300 ºC leads to the highest methane yield. Thus, we assume for our system modelling, that the methanation reactor with jacket or internal cooling works isothermally at 290 ºC. The product composition of such a model agrees well with the available steady-state experimental data.

4. Results and discussion

A sensitivity analysis is carried out to study the effects of utilization factor and the electrical heating on the system performance. As mentioned in the introduction, if the designed heat exchanger network cannot preheat the SOEC feeds to the preferred temperature, the electrical heating, which is frequently used for experimental setups to keep stable operation, must be employed. When tuning the temperature gradient of SOEC, the amount of electrical heating varies and is determined by the heat cascade.

4.1 Effect of utilization factor and electrical heating on the system performance

For the sensitivity analysis, the temperature different between the SOEC inlet and outlet is tuned between 0 and 120 ºC for three fixed utilization factors. The performance of the practically-feasible operating points is illustrated in Figure 4a. With a utilization factor between 60 % and 80 %, the HHV efficiency is theoretically beyond 80 %. The utilization factor has significant impact on the system efficiency (over 85 % for 80 % fuel utilization), as the higher the utilization factor the less steam generation and superheating is required.

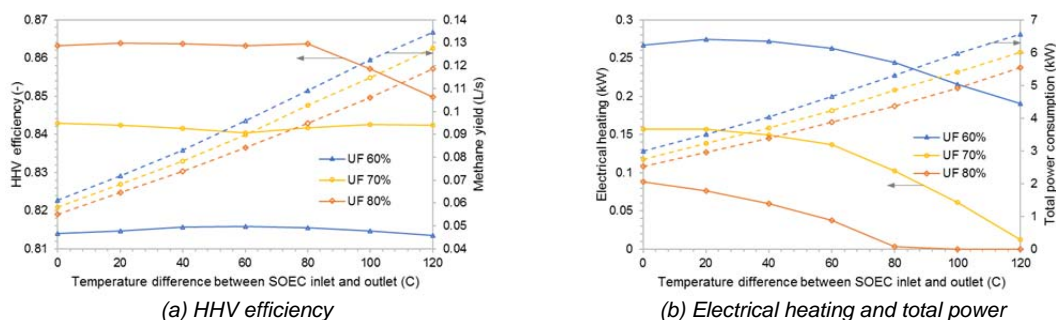| (a) HHV efficiency | (b) Electrical heating and total power |

Figure 4: Sensitivity analysis with respect to the cell temperature gradient and utilization factor (no heat loss considered, cell feed temperature 700 ºC, atmospheric pressure)

For investigating the effect of electrical heating, the temperature difference between SOEC inlet and outlet is increased so that the power consumed by external electrical heating is reduced, as is shown in Figure 4b. It is interesting that the external electrical heating almost does not affect the system efficiency (Figure 4a), as the amount of electricity for electrical heating is "equivalently" to that imposed to the SOEC itself. For the cases of 60 % or 70 % fuel utilization, the heat balance of whole system cannot be closed without electrical heating. While with an 80 % fuel utilization, the whole system can reach heat autonomy with no electrical heating (Figure 4b) at a SOEC outlet temperature of 780 ºC. At such a point, heat exchanger networks without electrical heaters may be derived, if the condensation heat of vapor can be partially utilized. A further increase in the SOEC outlet temperature over 780 ºC leads to a significant decrease in the system efficiency, since the SOEC outlet is "overheated" inside the cell from the perspective of heat integration, and the additional heat converted from electricity inside the cell goes across the pinch point and releases to the environment (cooling water). As above concluded, since external electrical heating does not affect the system efficiency, why is it important to minimize or even remove the electrical heating? This is mainly due to two reasons: (1) the frequent failure of electrical heater decreases the system reliability, and more importantly, (2) moving external electrical heating inside the cell itself can boost the product yield (Figure 4a). With the same feed temperature, utilization factor and SOEC hardware, the CH_4 yields for all cases in Figure 4 are doubled when the maximum allowed temperature gradient of 120 ºC along the cell is reached. When imposing larger current to SOEC, the gas temperature along the flow direction increases, while, by adapting the feed flowrate to reach the targeted fuel utilization, the resulting operating voltage varies only within a limited range, which leads to a boost of the production rate at almost no cost of efficiency.

4.2 Preliminary design of the system layout

For the given design specifications, the grand composite curves with or without consideration of vapor condensation (Figure 5) illustrates that the system can sufficiently reach heat autonomy, since, even without utilizing the vapor condensation heat, the heat available from the SOEC outlet is sufficient to close the heat balance. Particularly, up to 80 % of the heat needed for water vaporization can be supplied by the methanation reaction, which makes the integrated system much more efficient than each separate system. Moreover, as illustrated in (Figure 5b), the heat utilization situation does not change at all when discarding the condensation heat. This is particularly because the dew point of the involved gas mixture is below 90 ºC, which is difficult to be utilized within this specific system. If the technologies, e.g., organic Rankine cycle, can be coupled to utilize these low-grade waste heat, the integrated system can be even more efficient.

For the small-scale integrated system, the available heat is expected to be utilized to a maximum level. However, as a feature of the SOFC system design, the modularization should remain. Thus, when designing the heat exchanger network for the integrated system, the heat utilization is first maximized in both subsystems and, afterwards, the opportunities for flexibly coupling the two subsystems are identified.

With such design considerations, the integrated system can be more flexible even without employing complex auxiliary equipment.
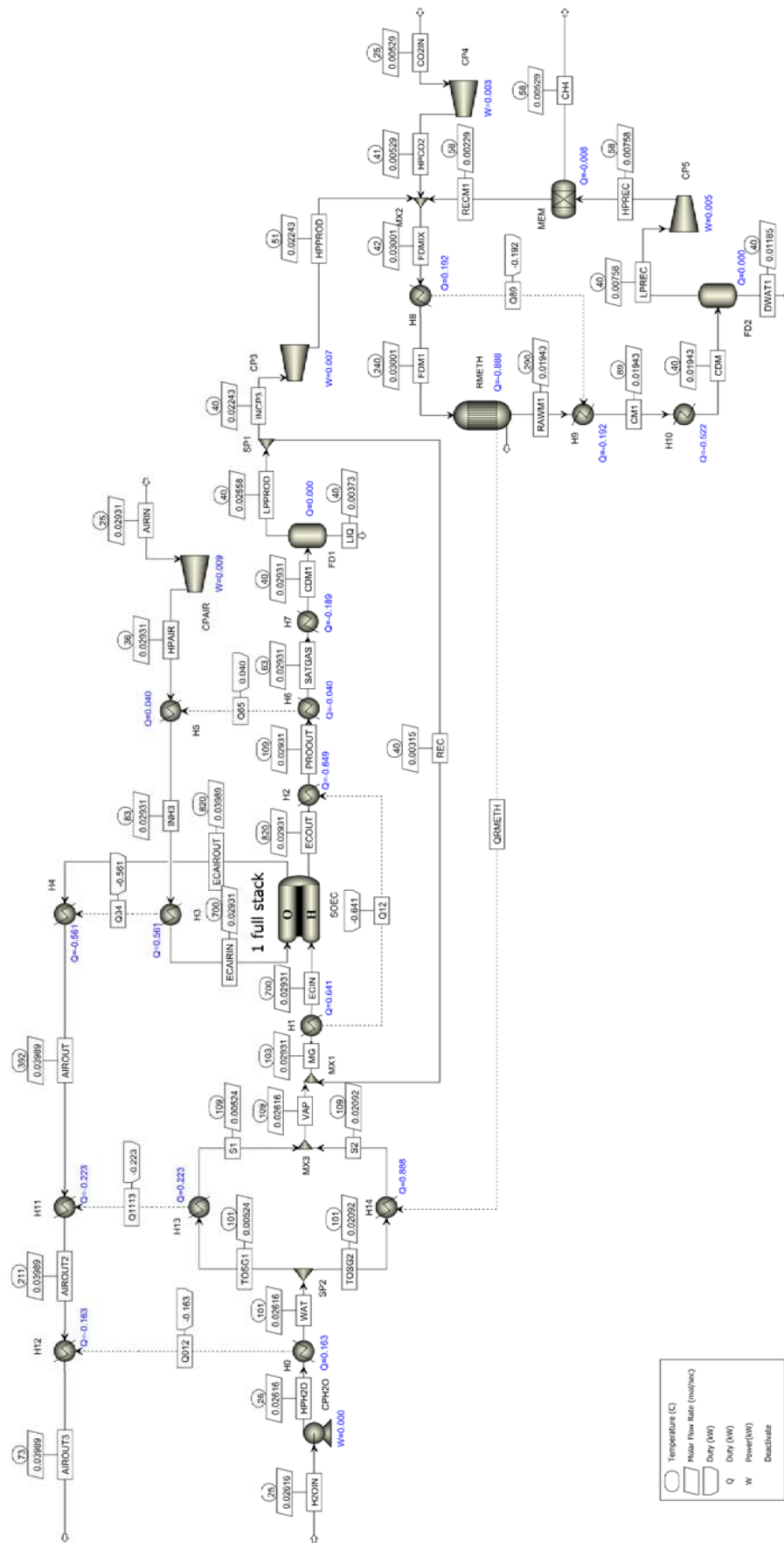
Figure 6: Preliminary proposal for the heat exchanger network design of the integrated system (H7 and H8 are directly cooled by the cooling water

A preliminary design of the heat exchanger network for the integrated system (Figure 6) is reached based on heat cascade. It is important to note that as the O_2 formed at the OER side largely increases the flowrate of the flowrates of the O_2 rich stream (ECAIROUT) and the available heat it carries. The utilization of this stream is essential to the design of SOEC subsystem. In the proposed HEN, the ECAIROUT first heats up the incoming sweep air to 700 ºC in H3 - H4, then the cooled air drives 20 % of the steam generation in H11-H13, and the remaining heat is eventually used for water preheating.
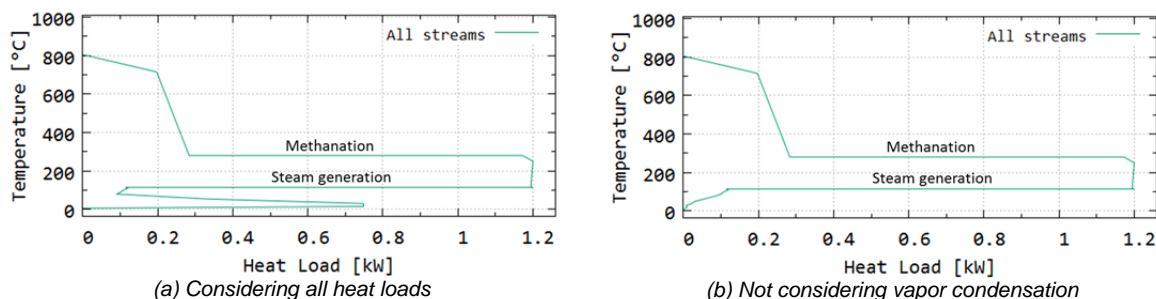

(a) Considering all heat loads   *(b) Not considering vapor condensation*

Figure 5: Grand composite curve for the design of a cell inlet temperature of 700 ºC, outlet temperature of 820 ºC and a fuel utilization of 80 % (no heat loss considered)

5. Conclusions

In this paper, the preliminary design of a small-scale, distributed power-to-methane demonstrator based on a full stack of 64 cells with 80 cm^2 activation area is investigated. The adiabatic performance of the electrolyzer is completely discussed with a calibrated quasi 2D model and insights different from isothermal experiments are obtained. A sensitivity analysis is performed to study the effects of utilization factor and the temperature gradient along the cell, which pinpoints the significant impact of different design points of the electrolyzer on the system performance. Afterwards, the preliminary design of the most favorable design point is performed to identify the heat integration opportunity and a specific heat exchanger network is derived. The major conclusions include:

- Practically, strong exothermic operation is preferred for the adiabatic operation of the electrolyzer. The temperature increase along the cell allows a larger current to be imposed without big increase in operating voltage, thus boosting the H_2 production rate with the same electrolyzer hardware.
- Given a fuel utilization, the electrical heating, if employed, has no effect on the system efficiency but limits the production rate. The electrical heating for normal operation should be avoided.
- The integrated system can be heat autonomous without electrical heating by properly selecting the electrolyzer operating point, thus increasing the reliability for regular operation.

References

Bernadet L., Gousseau G., Chatroux A., Laurencin J., Mauvy F., Reytier, M., 2015. Influence of pressure on solid oxide electrolysis cells investigated by experimental and modeling approach, International Journal of Hydrogen Energy, 40(38), 12918-12928.

CHBC, 2017. Power-to-gas white paper: The case for hydrogen, <californiahydrogen.org/sites/default/files/>, accessed 29.03.2017.

Founti M., 2016. Power-to-gas concept and overview of HELMETH project, NTUA Dissemination Event: "Energy Storage Technologies: Focus on Power-to-Gas Technology".

Kotisaari M., Thomann O., Montinaro D., Kiviaho J., 2016. Evaluation of a SOE Stack for Hydrogen and Syngas Production: A Performance and Durability Analysis, Fuel Cells, doi: 10.1002/fuce.201600166.

Menon V., Fu Q., Janardhanan V.M., Deutschmann O., 2015. A model-based understanding of solid-oxide electrolysis cells (SOECs) for syngas production by H_2O/CO_2 co-electrolysis, Journal of Power Sources, 274, 768-781.