Synthetic natural gas via integrated high-temperature electrolysis and methanation: Part I—Energy performance

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ABSTRACT

In this two-part paper the production of synthetic natural gas (SNG) through integrated plants featuring high temperature electrolysis and subsequent syngas methanation is analyzed. Part one focuses on plant configuration and performance evaluation. Part two focuses on cost for an economic assessment.

Two different ways to produce SNG have been analyzed: the first option features a plant that integrates steam electrolysis with methanation (Sabatier reaction); the second one considers co-electrolysis of water and carbon dioxide coupled with TREMP™ (Topsøe recycle energy-efficient methanation process). In both cases high temperature electrolysis with solid oxide cells (SOEC) technology has been employed.

A power input of 10 MWe was taken as the DC electricity input for both plant SOEC generators, based on power-to-gas plants now under construction in Europe. Sensitivity analyses were used to evaluate the impact of selected operating parameters on the plant performance. Especially the pressurization of the SOEC brings a reduction of the overall electrical input required to run the plant. By operating a pressurized SOEC, post-electrolysis syngas compression (that would be required otherwise because methanation takes place at ~33 bar) is partly replaced by liquid water pumping before electrolysis. Thermal integration based on the pinch analysis methodology was also applied in order to calculate the minimum external (thermal) energy requirement. Notably, most of the heat required for vaporizing and super-heating the electrolysis water can be recovered from the exothermic methanation section. Hence, a good thermal integration is available between SOEC and syngas upgrade catalytic section. This boosts the electricity-to-SNG efficiency to values as high as 80%.

The co-electrolysis plant shows a LHV efficiency of 81.4% that is more than five percentage points higher than the steam electrolysis case (76%): notably exothermic in-stack methanation – that occurs in the case of high pressure co-electrolysis assessment – allows for a reduction of the electricity input to the SOEC for the same amount of syngas produced among the two plants.

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1. Introduction

Natural gas (NG) is a major primary fuel in global economy, contributing to roughly 21% of total primary energy consumption [1]. The final use of NG is predominately in the industrial and residential/commercial sector, with almost an equal share between them. Transport is instead the only major end-use sector not widely penetrated by this fuel yet, despite the existence of viable technology already in the market (for instance, a large fleet of NG-fired engines for car and trucks are available from the automotive company FCA [2]). However, NG could become soon widespread in the road transportation sector as more public acceptance is gained, a wider network of re-fuelling stations of compressed natural gas (CNG) is established, and reductions of green-house gas (GHG) emissions in the transportation sector become more stringent. Despite the potential establishment of golden age of natural gas due to the exploitation of unconventional gas reserves [3–4] (shale gas, tight gas and coal-bed methane), numerous hurdles need to be overcome, especially environmental concerns associated with its extraction. Pathways to produce synthetic (or substitute) natural gas starting from renewable energy sources are thus relevant to decarbonize all those energy sectors heavily depending on fossil gas.

In 2011, much of the new installed (electric) capacity in Europe came from RES1: solar PV installed 21,000 MWe (46.7% of total new

1 Note that a distinction between net capacity installed and actual energy produced is especially relevant when comparing RES with fossil-fuel plants. For instance, for North America the capacity factor of NG-fired plants, wind and PV-solar is on average around 85%, 35% and 20%, respectively.
In order to store large amounts of surplus electricity for long periods and to balance seasonally RES electric production, chemical storage (or, more appropriately, conversion) in synthetic fuels might represent one of the most convenient ways [8]. The possibility to produce synthetic natural gas or liquid fuels (e.g., hydrocarbons or alcohols) through electrolysis and chemical processes synthesis was already studied [9–12].

Focusing on the “Power-to-Gas” pathway, low-priced surplus electricity is used to feed electrolysers that are able to produce a syngas consisting of either pure hydrogen or a mixture of H2 and CO, starting from water or a mixture of H2O and CO2 as feed reactants. A catalytic conversion of the syngas, which can react
with carbon monoxide or carbon dioxide to produce synthetic natural gas (SNG) is pursued afterward [13–15]. In Europe there is a great interest on power-to-gas solutions to couple electricity from wind with electrolysis and synthetic fuels production [16–21]. Recently, Audi established a 6 MW eplant for SNG production based on electrolysis [22]. A potential advantage of SNG production through power-to-gas compared to hydrogen production – that needs the electrolysis step only – is clearly that an existing distribution infrastructure for natural gas already exists. Also, the automotive sector has already vehicles with engines fired with NG. So the burden of a hydrogen economy with new infrastructure and new technology to be developed would be avoided.

Regarding electrolysis, there are two mature and commercially available technologies. The first one is represented by alkaline electrolyzers, whose stacks and cells are based on a liquid electrolyte (usually an aqueous solution with 25–30 wt% of KOH) operating at a temperature around 60–90 °C. The other technology is represented by PEM (proton exchange membrane) electrolyzers, characterized by an operating temperature of 40–80 °C and higher current densities (compared to alkaline), that use a polymer electrolyte membrane as a medium of ion transfer. Polymer membranes (such as Nafion™) are typically used because of its oxidation and thermal resistance. A review describing outlines, research, development and industrialization of these two electrolysis technologies is available in nuclear hydrogen production handbook [23].

A promising technology is the one that involves solid oxide electrolysis cells (SOEC). The operating temperature (700–900 °C) of this device is higher than the above mentioned technologies. As electrolyte material, zirconia stabilized with yttria (YSZ) is typically used, but also alternative materials have been analyzed. Concerning the solid oxide cells, reviews of possible choices regarding materials and cell configuration are available in literature [23–26]. The SOEC technology has been widely developed and studied with experimental tests at Risø DTU in order to characterize cells from the standpoint of performance and durability [27–35]. Also, at INL (Idaho National Laboratory) some investigations on SOEC have been performed, especially in order to evaluate a large-scale hydrogen (or syngas) production coupling the high temperature electrolysis (HTE) with nuclear energy [36–39]. In other works, some CFD models have been presented in order to simulate thermal, chemical and electrochemical behavior of single cells or multi-cell stacks [40–43]. Energy and economic analyses of the systems involving high temperature electrolysis processes have been performed, especially in order to define the heat management of the system [9,44–48]. Potential benefits of high temperature electrolysis are well summarized in literature [48–49].

In the work of Gahleitner [50] numerous power-to-gas pilot plants have been reviewed. The work deals with both hydrogen and SNG production plants. All the reported operating plants are based on low temperature electrolysis technologies (Alkaline and PEM).

In the open literature, the coupling between SOEC and Fischer–Tropsch process in order to convert electricity into hydrocarbons has been analyzed [9,33].

In this work a thorough analysis of two different process configurations for integrated high temperature electrolysis and synthetic methane production is assessed. Either H₂O or both H₂O and CO₂ are converted into hydrogen or syngas in integrated high temperature (SOEC) electrolysis and catalytic methanation plants. The energy performance comparison between the system that couples steam electrolysis to methanation, and the one which considers co-electrolysis of steam and carbon dioxide is systematically assessed for the first time with particular care to the thermal integration of each propose plant design.

Modeling of these plants has been performed using Aspen Plus™ software. The results have been obtained with a zero-dimensional model. This represents, especially for the SOEC section, a simplifying assumption which does not take into account thermal gradients along the stack as well as the impact of local kinetics. Both these factors may cause difference in results between the model and the real system. Then a thermal integration, in order to maximize overall plant efficiency, has been

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**Fig. 1.** Power-to-gas pathway through both low-temperature (LT) and high-temperature electrolysis devices. Low-priced surplus electricity from intermittent RES is fed to electrolyzers providing the necessary energy to bring H₂O (and CO₂) in a reduced state. In this way, renewable electricity can be effectively stored in large amounts in a chemical fuel (H₂ or a syngas). With LT-electrolysis (e.g., PEM and alkaline electrolyzers) H₂ only is produced, which can be employed for FC vehicles or alternatively stored in the NG gas distribution infrastructure to some extent. Ultimately, H₂ could be also used to produce power back a peak loads. Concerning the production of synthetic methane, with water (LT) or steam (HT) electrolysis, CO₂ is injected and mixed with H₂ before methanation. Alternatively with HT-electrolysis based on SOEC, co-electrolysis of carbon dioxide and steam is also possible. CO₂, when co-fed with steam to the stack, acts indeed as reactant for the electrochemical reactions and/or is converted internally via shift reactions to yield more steam. Syngas available can be converted to SNG and finally feed into distribution lines. The benefits of a coupled high-T Electrolysis and methanation process are investigated in this work.
made using the Pinch analysis methodology. In Fig. 1 the integration of gas and electricity networks thanks to electrolysis and particularly the power-to-gas pathway via SOEC is outlined.

2. Energy fundamentals of SOEC systems

In this section, the energy fundamentals required to understand the behavior of a solid oxide electrolysis cell are summarized and thus a consistent energy model of the SOEC plant is developed.

2.1. Thermodynamics of high-temperature steam and carbon dioxide electrolysis

The working principle and main reactions involved in the electrochemical dissociation of H2O and CO2 are briefly analysed. In solid oxide electrolysis cells (SOEC), the electrochemical steam reduction takes place at the cathode side:

\[ \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + \text{O}_2^- \]  

With co-electrolysis, carbon dioxide reduction must be also taken into account:

\[ \text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{O}_2^- \]  

At anode side, the following charge transfer reaction takes place:

\[ \text{O}_2^2^- \rightarrow \frac{1}{2}\text{O}_2 + 2e^- \]  

Faraday’s law of electrolysis expresses that reactant consumption in an electrochemical cell related to the current flowing through it (which we also refer to call as “faradic current”):

\[ \eta_R = \frac{i_F}{n_F} = \frac{jA}{n_F F} \]  

SOEC reversible voltage can be expressed as:

\[ V_{\text{rev}} = \frac{\Delta \bar{G}}{2F} \]  

Instead of number of electrons (nF) it has been put a value of 2, because both for steam and carbon dioxide reduction reactions, two electrons are involved. The fraction of inlet reactant molar flow which is effectively undertaking electrochemical reactions (\( \eta_R \)) is related to the total inlet molar flow (\( \eta_{\text{in}} \)) through the following equation:

\[ \eta_R = \eta_{\text{in}} \times \text{RR- RU} \]  

where RU (“reactant utilization”) is the fraction of reactant which effectively reacts in the stack, while RR (“reactant ratio”) is the reactant fraction of the inlet molar flow rate (this factor takes into account that the inlet feed stream to the SOEC must contain some fraction of H2 to avoid re-oxidation of the ‘fuel’ electrode; generally this is accomplished by recirculating a fraction of the cathode exhaust to the inlet).

Once moving away from the open circuit condition, the relationship between voltage and current in the electrochemical cell (polarization) is affected by non-linear transport phenomena (e.g., mass transport). For the remaining energy considerations of this section, a simplifying assumption is made by assuming a linear relationship between voltage and current density (i.e., a linearization of the polarization curve). The angular coefficient of this first order curve is the area specific resistance (ASR), defined as:

\[ \text{ASR} = \frac{V_{\text{op}} - V_{\text{rev}}}{j} \]  

where \( V_{\text{op}} \) and \( V_{\text{rev}} \) are the stack operating voltage and the reversible voltage, respectively. In this way, it is possible to derive the following expression for the operating voltage as a function of the current density:

\[ V_{\text{op}}(j) = V_{\text{rev}} + \text{ASR}(T,p)j \]  

Note that in reality the ASR is influenced by materials used for electrodes and electrolytes, respectively, geometrical features both macroscopic and microscopic and of course operational parameters such temperature, pressure and inlet gas composition.

The operation of a solid-oxide stack in the electrolysis mode is different than operation in the fuel-cell mode for several reasons, aside from the obvious change in the direction of the electrochemical reaction. From the standpoint of heat transfer, the fuel-cell mode typically requires an excess of air flow rate (with respect of stoichiometric amount for electrochemical reactions) in order to prevent overheating of the stack. Exothermic fuel oxidation and heating due to irreversibility phenomena make for heat generation within the fuel cell stack. Conversely, in the electrolysis mode, the steam and/or carbon dioxide reduction reaction is endothermic. Therefore, depending on the operating voltage, net heat generation within the stack may be negative, zero, or positive meaning the stack works as heat sink, as thermo-neutral device and as heat source respectively. Generated heat flux (W/cm^2) is produced by the cell (available heat) and is given by:

\[ \dot{q}_{\text{gen}} = \frac{j}{2F} \text{ASR} = j(V_{\text{op}} - V_{\text{rev}}) \]  

Referring again all terms to the inlet mole flow which effectively reacts, and considering Faraday’s law for electrolysis, the reaction heat flux consumed by the cell (needed heat) can be expressed as follows:

\[ \dot{q}_R = j \frac{2}{F} T \Delta \bar{\xi} \]  

In the electrolysis mode, the net heat flux is negative for low operating voltages, increases to zero at a voltage called “thermoneutral voltage” or “thermoneutral voltage”, and is positive at higher voltages and current densities. It is possible to define the therm-neutral voltage as follows:

\[ V_{\text{in}} = \frac{\Delta \bar{H}}{2F} \]  

Considering Eq. (8) it is possible to express current density at thermoneutral condition as:

\[ j_{\text{in}} = V_{\text{in}} - V_{\text{rev}} = \frac{\Delta \bar{H} - \Delta \bar{g}}{2F} = \frac{1}{\text{ASR}} \frac{1}{2F} T \Delta \bar{\xi} \]  

With reference to Eq. (11), also in this case \( \Delta \bar{H} \) is referred to the inlet mole flow which effectively reacts.

Considering again reaction heat flux \( \dot{q}_R \), it can be written as:

\[ \dot{q}_R = j \frac{2}{F} T \Delta \bar{\xi} = \frac{j}{2F} (\Delta \bar{H} - \Delta \bar{g}) = j(V_{\text{in}} - V_{\text{rev}}) \]  

Setting \( V_{\text{op}} = V_{\text{in}} \) and comparing reaction heat flux \( \dot{q}_R \) with generated heat flux \( \dot{q}_{\text{gen}} \), they have the same expression, i.e., they are equal and opposite (in the thermo-neutral conditions). In the fuel-cell mode the net heat flux is always positive and increases rapidly with current density. In the electrolysis mode, the net heat flux is negative for low operating voltages, increases to zero at the “thermoneutral” voltage, and is positive at higher voltages and current densities.

2.1.1. Co-electrolysis reactions scheme

In the co-electrolysis, the fuel electrode shows the presence of a reacting mixture composed of H2O, CO2 (reactants) and H2, CO
sulfur, halogen and siloxanes compounds should be taken out [51]. CO2 could be also sourced from biomass syngas, which would pose cleaning issues similar to that of biogas (even if chloride compounds, tars and metals are more relevant compounds to be removed). In a more developed scenario with CCS in the industry and power generation sector, CO2 from pipelines should already meet quite stringent quality criteria and be (almost) ready to feed an SOEC [52].

### 3.2. General overview of integrated SOEC-methanation plants

In this study the integration of high-temperature electrolysis with subsequent syngas methanation to produce SNG is investigated. In particular, two different plant layouts based on steam electrolysis only and co-electrolysis of steam and carbon dioxide in a SOEC plant are considered.

In both cases, downstream methanation of the syngas produced in the SOEC plant is carried out to yield stream of almost pure methane that is suitable (in term of density and heating value) to be injected in the NG grid.

In Figs. 2–3 the two different processes are outlined. In both cases the reactant water is pumped and then heated up through a steam generator. The SOEC is operated at high pressure (33.1 bar) and at a temperature of 850 °C, according to literature data [8,27,31,33,35].

A hydrogen mole fraction of 10% is always guaranteed for the cathode stream feeding the SOEC through a recirculation system, in order to avoid Ni re-oxidation in the electrode [35].

In the steam electrolysis case, CO2 is compressed and cooled down to the methanation inlet temperature (220 °C); then it is mixed with H2 from SOEC in order to have a syngas (H2 + CO2) able to produce methane in the subsequent section. In the co-electrolysis system, carbon dioxide is a reactant sent directly to the SOEC. CO2 is compressed and heated up to the SOEC operating temperature and co-fed to the SOFC with steam. A syngas consisting of H2 and CO is obtained for downstream methanation.

In both plants, the SOEC exhaust gases are cooled down. The cathode outlet is cooled to the methanation inlet temperature, whereas the anode outlet stream (pure oxygen) is cooled down to 35 °C thus accounting as additional heat source for thermal integration in the plant-wide heat-exchanger network. The syngas entering the methanation section (either H2O–H2–CO2 for steam-electrolysis, or H2–CO–CO2–H2O–CH4 for co-electrolysis) flows through a cascade of four adiabatic reactors with intercoolers. The resulting outlet gas stream is chilled to condense and separate water that can be recycled back to the SOEC. Dry synthetic natural gas (SNG) is further cleaned by passing it through a molecular sieve that removes residual H2O and CO2 [53].

Finally, SNG is compressed to 60 bar and eventually blended with N2 to meet pipeline prescriptions about SNG quality or LNG production requirements.

### 3.3. SOEC

Pressurized stack operation (33.1 bar) is analysed in this work mostly because methanation is favored at high pressure and generally employed in commercial reactors (also to reduce volume size). Having a pressurized SOEC is beneficial because of...
thermodynamic considerations: an atmospheric SOEC would require energy-intensive syngas compression upstream of methanation that is partially replaced by much less energy consuming water pumping in the pressurized option. Also, atmospheric SOEC with post-electrolysis syngas compression would require cooling far below the 220 °C required at the first methanation reactor.

3.3.1. Area specific resistance
In our work we assumed the SOEC plant operates with planar-type Ni–YSZ supported cells [31,32,35]. A dependence of the ASR as a function of temperature and pressure was established. Then, estimation was made starting from open literature data based on the work of Rise Laboratory and DTU (Technical University of Denmark). ASR increase due to switching from single cell to a stack configuration (i.e., considering essentially the contribution of interconnector + contact resistances) was derived [35]. The dependence of ASR for a varying temperature both for steam electrolysis and co-electrolysis was estimated [31]. Finally, the behavior of ASR at different pressures for steam electrolysis was extrapolated [32] (the same trend was then also applied for co-electrolysis). By fitting and interpolating the above-mentioned literature data, an ASR relation for steam and co-electrolysis was derived in the following form:

\[
\text{ASR}(p, T) = D \exp(-B \cdot T) \exp(-C \cdot p)
\]

(19)

where \( D, B \) and \( C \) are constant values summarized in Table 1.

Assuming for a given plant a fixed value of total Faradic current, i.e., a term proportional to the plant size and its productivity, the total installed active area is the following:

\[
A = \frac{I_f}{J}
\]

(20)

So, varying ASR has impact on active area, i.e., on economics of the system because a portion of the total capital cost of a SOEC plant must be attributed to the stack active area to be installed.

Relation between ASR and pressure has not been yet clarified, especially at high pressure values (from 10 bar up). So this estimation may be optimistic or at least affected by errors. In present work this uncertainty will be taken into account by taking an average value between ASR given by the estimation above described (lower value) and another one (higher value) in which pressure contribution will be not considered (i.e., by setting in equation (19) \( C \) equal to 0).

The overall ASR of a SOEC stack depends on operational parameters such as pressure, temperature and inlet gas composition. By assuming to operate at fixed thermodynamics conditions \( (p, T \) and cathode inlet composition) and potential (e.g., thermoneutral voltage), the stack ASR (that is a way to measure the electrochemical and electrical performance of the SOEC) has an impact on the economics of the system rather than on its efficiency. Considering Eq. (8), different values of ASR (that might correspond to employing cells and/or stack designs from different manufacturers) imply different allowed values of current density to yield the same desired operating voltage. In other words, if the stack is operated at constant voltage the ASR is a performance figure-of-merit that specifies how many electrons per cm² of active area can flow through the cell to produce a certain polarization.

3.3.2. Thermal management of an SOEC stack
The strategy for thermal management of an SOEC stack is less straightforward than for an SOFC because high-temperature electrolysis can result in either exothermic, endothermic or thermoneutral operation depending on the operational parameters of the SOEC.

As mentioned before, the SOEC can operate within three different conditions: below, above or equal to thermoneutral voltage. Electric power can be expressed as:

\[
W_{el} = V_{op} I_f
\]

(21)

By combining together Eqs. (20) and (21) with the First law of thermodynamics it results that:

\[
V_{op} = V_m - \frac{\phi}{J}
\]

(22)

This last expression suggests that, once thermoneutral voltage and Faradic current are fixed or established, a relation between operative voltage \( (V_{op}) \) and net heat flux \( (\phi) \) occurs. Then, three possible conditions can be identified:

- If \( V_{op} = V_m \) (thermoneutral condition) then \( \phi = 0 \), confirming that thermoneutral voltage makes the net heat flux equal to zero.
- If \( V_{op} < V_m \) (“sub-thermoneutral” condition) then \( \phi > 0 \). In this case the system requires a certain heat flux to allow isothermal operation: for now it can be supposed that is provided electrically. This last aspect will be further discussed.
- If \( V_{op} > V_m \) (“over-thermoneutral” condition) then \( \phi < 0 \). Thus, heat flux must be rejected for isothermal electrolysis.

3.4. Methanation
In this section CO and CO2 are hydrogenated according to the methanation reactions, both favored by low water content and high pressure [54–57]. These Reactions – (15) and (16) – have been already mentioned before in another context (the chemical model of co-electrolysis). It can be seen from these equations that CO hydrogenation is more exothermic than CO2 hydrogenation.

The Haldor-Topsoe TREMP™ (“Topsoe Recycle Energy-efficient Methanation Process”) technology was considered in our work to design and model the syngas methanation section. Generally, TREMP™ process is the final stage of a system designed to produce SNG starting from coal or biomass. In such plants, the gasification of a solid fuel, with an air separation unit to provide oxygen to the gasifier, is followed by chemical processes as a sour shift, an acid gas removal unit and sulfur recovery [54]. In our case, the methanation unit is placed downstream of the SOEC and upgrades the syngas that is already clean and in the right stoichiometric amount to methane.

In order to achieve a product with the highest methane content, it is important that the feed gas for the methanation section has a composition with a proper stoichiometric feed ratio of the reactants, (i.e., CO, H2 and CO2), which is defined as following [56]:

\[
\text{FEED} = \frac{[\text{H}_2] - [\text{CO}_2]}{[\text{CO} + [\text{CO}_2]]} = 3
\]

(23)

This concept is valid also for steam electrolysis systems. Indeed, mixing hydrogen (but not CO) from cathode outlet with CO2 from an external source, a particular case of feeding stream is realized (those without carbon monoxide). Solving Eq. (23) with [CO] set equal to 0, hydrogen to carbon dioxide ratio of 4 is obtained, allowing a stoichiometric Sabatier Reaction (16). Reactors in Fig. 2

<table>
<thead>
<tr>
<th>Steam electrolysis</th>
<th>Co-electrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [Ω cm²]</td>
<td>35.71</td>
</tr>
<tr>
<td>B [K⁻¹]</td>
<td>0.0057</td>
</tr>
<tr>
<td>C [bar⁻¹]</td>
<td>0.0217</td>
</tr>
</tbody>
</table>

Table 1: Constant values used for the estimation of ASR as a function of pressure and temperature. These values were derived from the interpolation of experimental data available in a temperature range of 750–850 °C, and for pressure up to 10 bar.
and Fig. 3 are assumed adiabatic, so exothermic reactions will cause a temperature increase along the reactor from inlet to outlet. Methanation reactions are favored by high pressure operation. In order to reach high methane concentrations (95–98%) in the final gas stream, it is necessary to use several methanation reactors connected in series with intermediate cooling in between [54].

In order to maximize the temperature increase across the first methanation step (i.e., to reduce recirculation), a combination of a non-Ni catalyst and a Ni catalyst is used allowing an inlet temperature as low as 220 °C against 320 °C usually considered [54].

As it will be discussed later, in an integrated high temperature electrolysis and methanation system, the heat recovered from the methanation unit (along with that available from syngas cooling downstream of the SOFC) can be effectively used to pre-heat the SOEC reactants.

In this work it has been supposed that for both systems the methanation technology and model are the same, despite TREMP™ is normally used for methanation of mixtures with low content of CO2.

3.5. Plants modeling

As written above, two plant structures are considered in the analysis: the first plant employs steam electrolysis followed by methanation via the Sabatier Reaction (15); the second plant option foresees instead co-electrolysis coupled with Methanation. In Table 2 the main assumptions made in modeling both plant are summarized.

3.5.1. Plant size

The SOEC plant requires a power input not only for the electric power directly involved in electrochemical reactions, but also to generate additional heat in case it is operated at sub-thermoneutral condition (i.e., \( V_{op} < V_{in} \)). Thus, the SOEC power input is expressed in the following form:

\[
W_{el} = \sum \eta_{out} n_{out} - \sum \eta_{in} n_{in} = \eta_{out} n_{out} - \eta_{in} n_{in}
\]  

(24)

Another relevant operating condition is represented when \( V_{op} > V_{in} \). According to SOEC thermodynamics, in this situation irreversible heat production is higher than reaction heat. Hence a certain quantity of thermal power must be rejected to ensure isothermal condition. A possible way is represented by using this exceeding heat for the reactant pre-heating (see Fig. 4). In this last case cathode inlet flow enters into the stack at a temperature lower than the operating one, in order to allow heat rejection.

In both steam electrolysis and co-electrolysis plants, the specified value of 10 MWe has been fixed adjusting the external water molar flow. This is the amount of power input fed to the SOEC electrolysis reactor.

3.5.2. Reactant utilization

The reactant utilization (RU) is expressed by the following equation:

\[
RU = \eta_{react} - \eta_{reactout} \quad \eta_{reactin}
\]

(25)

In a stack with cathode recirculation, the RU can be actually evaluated including or not the recirculation. In the first case we define a “global reactant utilization” (\( RU_g \)), otherwise “stack reactant utilization” (\( RU_s \)) is considered.

The concept of RU is complicated in the co-electrolysis case because of the presence of chemical reactions. Considering WGS Reaction (17) it is clear that this reaction does not imply a variation of RU, because the reaction is equimolar on both directions (direct or inversion reaction). On the other hand, the CO hydrogenation implies the reactions of 3 moles of an “electrolysis product” (hydrogen) and the production of one mole of an “electrolysis reactant” (steam). A similar consideration can be done for methanation of CO2.

Fig. 2. Steam electrolysis plant layout: carbon dioxide is injected and mixed with hydrogen downstream of the SOEC. The steam generator has been divided into three stages: economization, evaporation and superheating. A cascade of adiabatic inter-cooled methanation reactors converts the syngas (\( H_2 + CO + H_2O \)) into SNG. Post-methanation cooling is outlined with two heat exchangers: HE 10 realizes a pre-cooling, whereas HE 11 condensates the water into the stream.
Thus, in this study we discriminate between the “stack RU” (RUs) and “electrochemical RU” (RUec). The first one considers the net balance of reactants at stack inlet and outlet (excluding recirculation, which is taken into account by “global RU”). The second one considers reactants involved in electrochemical reactions only. Note that RU mentioned in calculation of parameter as $V_{rev}, \Delta \bar{G}, V_{in}, \Delta \bar{H}, \varphi_h$ must be RUec, because that one related to electrochemical reactions. The relationship between RUec and RUs is affected by operational temperature and pressure, which determine chemical equilibrium of methanation reactions and consequently consumption of hydrogen and production of water involved in these reactions. The value in Table 2 is referred (in both plant) to the variation of reactant concentration between cathode inlet and cathode outlet excluding recirculation, i.e., the RUs.

3.5.3. Recirculation rate and molar flow rates

In steam electrolysis, it is possible to establish an analytic correlation between recirculation rate (i.e., the ratio of recycled exhaust gas to the total exhaust gas), reactant utilization and hydrogen mole fraction in cathode inlet flow. This relation can be expressed considering molar balances applied to the SOEC control volume in Fig. 4.

$$y = \frac{1}{1 + (Z \times RU)}$$  \hspace{1cm} (26)

where $y$ is the recirculation rate and $Z$ is a parameter taking into account the imposed hydrogen mole fraction at cathode inlet (10%), defined as follows:

$$Z = \frac{1 - [H_2]}{[H_2]}$$  \hspace{1cm} (27)
In co-electrolysis plant, the equilibrium reactor introduces non-linearity issues in the mass balance calculations that does not allow for a strict analytical evaluation of the recirculation rate. Thus, a hydrogen mole fraction of 10% was reached by varying iteratively the recirculation rate of cathode outlet.

Another constraint of the SOEC model is represented by Eq. (23). Considering that water molar flow rate has already been varied in order to have a stack power of 10 MWe, for both plants the target for FEED is reached changing carbon dioxide molar flow. In steam electrolysis is again possible to establish an analytic correlation, this time between CO2 and H2O molar flow. Also in this case this relationship is obtained just applying molar balances to the SOEC, and depends on RU and Z.

\[
\pi_{\text{CO}_2} = \frac{1 + Z\text{RU}}{4(1 + Z)}\pi_{\text{H}_2\text{O}} 
\]

\(\pi_{\text{H}_2\text{O}}\) is the steam molar flow at cathode inlet.

In co-electrolysis, again it is not possible to find an “a priori” analytic correlation. Then, \(\text{FEED} = 3\) is obtained adjusting \(\text{CO}_2\) mole flow at cathode inlet in an iterative way.

3.5.4. SNG quality

Before pumping the obtained SNG into the transport infrastructure, some technical specifications must be verified. In this work prescriptions established in Italy (by “Snam Rete Gas”) for pumping natural gas into pipelines have been used [58]. The main constraints regard three parameters that will be following discussed:

- Gas gravity
- Wobbe index
- Higher heating value of produced SNG

Gas gravity is the ratio between densities of produced SNG and air, both calculated at “standard conditions”, i.e., 101,325 Pa and 288.15 K [58].

\[ GG = \frac{\rho_{\text{SNG}}}{\rho_{\text{air}}} \] (29)

\(\rho_{\text{air}}\) was set to a value of 1.22 kg/m^3 assuming a mole mass equal to 28.84 kg/mol. Wobbe index is expressed by the following equation:

\[ WI = \frac{\text{HHV}}{\sqrt{GG}} \] (30)

HHV is the higher heating value of SNG.

During the evaluation of HHV related to the pipeline prescriptions, only methane (and not hydrogen) contribution was prudently considered, despite also hydrogen is a fuel. Acceptability boundaries for these parameters are summarized in Table 3.

There are also other prescriptions on natural gas composition [58], e.g., regarding mole concentration of components as oxygen, carbon dioxide, water (in terms of dew point of the mixture at a relative pressure of 7000 kPa), sulphuric molecules, particulate and liquid hydrocarbons.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>34.95–45.28</td>
<td>47.31–52.33</td>
<td>0.5548–0.800</td>
</tr>
</tbody>
</table>

It has been verified that produced SNG has too low density, and consequently too low gas gravity. This is explainable considering that SNG is essentially composed by methane and hydrogen, and for this reason has a too low density. So it is necessary to “correct” SNG blending it with a diluent. Nitrogen has been used, but it is not the only possible choice. Dilution of SNG with \(N_2\) causes lowering of HHV and Wobbe index, which still after correction must be comprised between acceptability boundaries. The target value is \(GG = 0.555\), obtained by varying nitrogen mole flow.

3.5.5. Pressure drops and BoP devices

Pressure drops in the integrated plants were attributed to the main components as described in the following. Due to uncertainties related to the heat exchanger network design, and consequently to the difficulty on establishing parameters as diameter of pipe, speed of fluid and friction factors, the overall pressure drop for water vaporization and subsequent steam superheating has been set as of 6% of the total inlet pressure [59].

For the SOEC electrolysis an operating pressure of 33.1 bar was instead set to allow for syngas at the methanation section at 32.4 bar [53]. A pressure drop of 0.7 bar for intercoolers involved in the process has been assumed [53]. Regarding the pressure drop for methanation reactors, an average value of 0.7 bar was chosen [53].

In order to realize the compression of water, carbon dioxide and SNG, pumps and compressors are required. They are characterized by isentropic efficiencies and performances of the related electric driving. Isentropic efficiency has been set to 0.75 for compressors [60] and to 0.8 for pumps. Electro-mechanic efficiency has a value of 0.95 for compressors and 0.9 for pumps. This last difference is related to the size of the electrical device, which is greater in gas compression case.

A large amount of electric energy involved in both plants requires an AC/DC conversion through a rectifier, which efficiency has been set to 0.98.

3.6. Thermal integration

In order to perform the thermal integration, the methodology of Pinch analysis was used [61–63]. In our plants there are constraints that have to be satisfied (e.g., temperature of reactants along the process) as well as a target function must be chosen for the network design, e.g., minimum of external energy demand or minimum of heat exchange area (which is usually considered proportional to the cost of heat exchanger, so involves economic issues). In this work the target is the minimization of external heat requirement.

In addition to stream flow temperatures, another constraint is the minimum temperature difference (\(\Delta T_{\text{min}}\)) between hot fluids (i.e., those which have to be cooled down) and cold fluids (i.e., those which have to be heated up). In this work, a \(\Delta T_{\text{min}}\) of 20°C was used [62].

Boundary conditions are referred essentially to modalities whereby the examined system realizes heat exchanges with external sources. For analyzed systems it has been supposed that for external heating an electrical source will be used, whereas for external cooling water at 15°C will be available. The pinch point is the point where there is the minimum value of temperature difference between hot and cold fluids.

4. Results

4.1. Sensitivity analyses of pressure effect on the SOEC

In this work a sensitivity analysis for both electrolysis systems (steam and co-electrolysis) has been performed in order to
evaluate the behavior of some key parameters when varying the SOEC operating pressure. In fact, pressurization is a key issue deserving some remarks, because of its effect on system thermodynamics, electrochemistry and economics.

4.1.1. Steam electrolysis

In Fig. 5 the trends with pressure of reversible voltage, thermoneutral voltage and current density at thermoneutral condition are shown. The reversible voltage shows a slight increase, due to the logarithmic effect of partial pressures on the $\Delta$G term in the Nernst equation [26,42,64,65]. The thermoneutral voltage is essentially constant, because enthalpy is basically not affected by pressure (both in ideal gases model and in Peng–Robinson state equation).

Looking at the Eq. (12) for thermoneutral current density, increasing pressure means a decrease of the numerator and simultaneously a denominator reduction, because it has been assumed that ASR is pressure affected. For low pressures there is an initial decrease of current density (up to approximately 8 bar) in which decrease of the numerator in Eq. (12) dominates and the minimum is reached. After, the drop of ASR becomes more relevant than the reduction of interval between thermoneutral and reversible voltage. Furthermore, a non-negligible role is played by the trend of the ASR as a function of pressure.

In Fig. 6 the overall electric power required as a function of SOEC pressure is presented. The higher the SOEC pressure, the lower the overall power required for compression (i.e., of total power) in the plant. As commented before, the inlet pressure of the syngas in the methanation section is fixed to ensure an optimized conversion rate. SOEC pressurization is more efficient (by almost 6 percentage points) as it replaces downstream syngas compression with much less energy intensive upstream water pumping.

4.1.2. Co-electrolysis

The impact of SOEC operating pressure on reversible and thermoneutral voltages as well as current density at thermoneutral condition has been analysed also (Fig. 7) for the co-electrolysis case. The trend of reversible voltage is similar to that of steam electrolysis. On the contrary, the thermoneutral voltage results decreased as pressures increase due to the presence of chemical reactions. Especially, the methanation reaction is favored at high pressure. Being an exothermic reaction, it brings a reduction of the overall $\Delta$H between stack inlet and outlet. According to Eq. (11) this aspect produces a lower $V_{tn}$ than with steam electrolysis only.

Current density is characterized by a monotonic decrease, because the drop of the term $V_{tn}$–$V_{rev}$ is predominant respect to the reduction of ASR with pressure. Obviously, considerations made for steam electrolysis on this last issue remain valid.

In Fig. 8 syngas composition at cathode outlet stream is shown. As expected, methanation is thermodynamically favored at high pressure. This fact is confirmed by the simultaneous decrease of H2 and CO. CH4 concentration reaches a value around 10% at 30 bar. This is coherent with the $\Delta$H drop increasing pressure. Considering that the final plant product is methane, its formation already in SOEC stack looks as an advantage. Furthermore, if a certain part of syngas entering into the methanation section is composed by methane, this allows avoiding recirculation of cooled output syngas at the first reactor. In systems with gasification of solid fuels inlet gas is essentially composed by H2 and CO, then reaction in the first reactor is very exothermic, so recirculation is required. But if CH4 is present, it plays the role of a diluent, lowering outlet temperature. According to our process simulations, at the selected pressure (33.1 bar), the methane mole fraction is high enough at the inlet of the first reactor to ensure an outlet temperature lower than 700 °C (upper value to avoid catalyst sintering). Thus, no...
recirculation is required. This is an advantage in terms of global efficiency, because methanation is more efficient and a recirculating compression (consuming electric power) is avoided.

Regarding electric power involved, the situation is equivalent to the steam electrolysis case and the trend of considered powers by varying pressure is similar. Therefore, from an energy efficiency standpoint, pressurizing SOEC for steam and co-electrolysis represents an advantage. Economic issues will be detailed discussed in the second part of this work (see part 2). For now, energy advantages of pressurization mean obviously economic advantages in terms of energy input savings. On the other hand, pressurized systems require more expensive devices, which may partly offset advantages linked to the higher efficiency. Furthermore, for co-electrolysis high pressure implies lower current density (at thermoneutral point), i.e., higher active area, under hypothesis of constant faradic current, according to Eq. (20).

4.3. Energy performance results

In Table 4 the gas composition in some key points for both analyzed plants is given. Concerning the cathode outlet composition, in steam electrolysis only hydrogen and water are present, whereas in co-electrolysis also carbon dioxide, carbon monoxide and methane are involved. Mole fractions for hydrogen and steam are respectively higher than carbon monoxide and dioxide, highlighting a larger quantity of H2O involved in co-electrolysis respect to CO2, due to the “feed constraint” (FEED = 3), which implies more water than carbon dioxide. The presence of methane confirms, for co-electrolysis, that methanation takes place already into the cathode. CH4 concentration is quite high, due to the cell operating pressure.

In co-electrolysis cathode outlet gas coincides with methanation inlet, whereas for steam electrolysis based system CO2 injection takes place between the stack and the methanation section, varying gas composition. For both systems the stoichiometric relationship between H2, CO and CO2 at methanation inlet is verifiable.

At methanation section outlet water content of the resulting mixture is high, because of the reactions stoichiometry. In steam electrolysis system water concentration is higher because only Sabatier Reaction (16) takes place. Thus, two moles of steam are generated per mole of produced methane.

With reference to the gas composition at plant outlet (i.e., before flowing into the pipeline), CH4 mole fraction is higher for co-electrolysis based plant, due to the methanation at cathode side. Indeed, considering the methanation section as control volume, hydrogen utilization is more or less the same for both systems (around 99%). But H2 concentration at methanation inlet is higher for steam electrolysis, because of Reactions (15)–(16) stoichiometry and CH4 presence for co-electrolysis. For steam electrolysis plant, after cleaning section hydrogen concentration is greater. As a consequence, higher H2 mole fraction implies lower gas gravity. Thus, a larger quantity of Nitrogen must be used to reach an acceptable SNG density. H2O is not present because it has been supposed that molecular sieve used for cleaning would be able to retain entirely steam traces. CO and CO2 concentrations are at the magnitude of ppm.

In Table 5 and Table 6 the main electrochemical and plant parameters are summarized. The SOEC reversible voltage is quite similar for both steam and co-electrolysis. This fact can be partly explained with similar values of ΔG for steam and carbon dioxide reduction at SOEC operating temperature [11]. Also chemical reactions (taking place in co-electrolysis) could have an impact on ΔG; however, similarity between ΔG for H2O an CO2 reduction seems to be a good explanation. Furthermore, electrochemical CO2 reduction is different for the two systems; this is another issue that has an impact on Voc.

Thermoneutral voltage is higher for steam electrolysis. The reason is essentially related to methanation, which takes place in
co-electrolysis and is strongly exothermic, causing a decrease of the enthalpy of reaction. Indeed part of reduction energy requirement is provided by this reaction.

The ASR is higher for co-electrolysis, as also reported in literature [31]. This aspect results also from approximations present in this work, as said before, for ASR estimation.

According to Eq. (7) expression for current density at thermoneutral point is:

\[ \text{\(j_{\text{th}} = \frac{V_{\text{tm}} - V_{\text{rev}}}{\text{ASR}}\) \] (31)

This value is much greater (almost doubled) in steam electrolysis case for the combined effect of a higher numerator and a lower denominator.

As said before, three kinds of reactant utilization have been recognized (electrochemical, stack and global RU). For steam electrolysis, obviously, electrochemical and stack RU coincide, because of the lack of chemical reactions. For co-electrolysis it results that electrochemical RU is greater than stack RU. This means that chemical reactions taking place at cathode side globally are characterized by product (i.e., H₂ and CO) consumption higher than reactant (H₂O and CO₂) production. This is true for methanation Reactions (15) and (16) whereas it is not for water gas shift equilibrium (18). Thus, to obtain a reactant consumption of 70% along the stack, a higher fraction of reactant must be involved in electrochemical reactions.

Faradic current is higher for co-electrolysis because of a greater electrochemical RU, according to Eqs. (4) and (6). Lower reactant ratio (RR) partly offset the previous consideration. Moreover, the fixed electrolysis power of 10 MWe can be expressed also as the product of thermoneutral voltage and faradic current. As foreseeable, if \(V_{\text{tm}}\) is lower, \(\text{\(i_{\text{F}}\)}\) will be greater.

Considering thermoneutral operating condition, a larger active area is required for co-electrolysis, according to Eq. (20). This aspect is further amplified by the higher faradic current.

<table>
<thead>
<tr>
<th>Cathode outlet (after the SOEC)</th>
<th>Methanation inlet feed</th>
<th>Methanation outlet stream</th>
<th>SNG outlet stream</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SE</td>
<td>CE</td>
<td>SE</td>
</tr>
<tr>
<td>H₂O</td>
<td>27.0%</td>
<td>25.1%</td>
<td>22.8%</td>
</tr>
<tr>
<td>CO₂</td>
<td>–</td>
<td>4.7%</td>
<td>15.4%</td>
</tr>
<tr>
<td>H₂</td>
<td>–</td>
<td>49.5%</td>
<td>61.7%</td>
</tr>
<tr>
<td>CO</td>
<td>–</td>
<td>10.2%</td>
<td>–</td>
</tr>
<tr>
<td>CH₄</td>
<td>–</td>
<td>10.5%</td>
<td>–</td>
</tr>
<tr>
<td>N₂</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

| Table 4 | Stream gas composition for different key points of the plant. “SE” and “CE” correspond to the “steam electrolysis” and “co-electrolysis” plants, respectively. |

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Main electrochemical and stack parameters for both analysed plants.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant</td>
<td>Steam electrolysis</td>
</tr>
<tr>
<td></td>
<td>(V_{\text{rev}}) [V]</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------</td>
</tr>
<tr>
<td></td>
<td>1.028</td>
</tr>
</tbody>
</table>

Cathode recirculation rate is higher for co-electrolysis, where hydrogen mole fraction at cathode outlet is lower. Indeed recirculation is done to ensure a hydrogen concentration of 10% at cathode inlet. Larger recirculation rate implies lower reactant ratio (RR), because recirculated gas is mostly composed by electrolysis products.

With reference to Table 6, recirculated water is obtained by condensation of the syngas flowing out from methanation section. Recycling this water is useful to avoid a too large consumption of demineralized water. Recirculation rate is higher in steam electrolysis case for a stoichiometric reason. Indeed in this plant the only methanation reaction taking place is CO₂ hydrogenation, i.e., Reaction (16), in which 2 mol of water are produced per obtained mole of CH₄. In co-electrolysis based plant both hydrogenation of CO and CO₂ happen, but the first one, i.e., Reaction (15), has a bigger weight in methane production because at cathode outlet CO concentration is higher than CO₂. Reaction (15) shows that one mole of water is produced per mole of CH₄. After the cooling syngas temperature is 35 °C, so almost all water condensates, whereas the remaining gaseous part is retained by the molecular sieve.

Moreover, it has been verified that Wobbe index and HHV are comprised into the acceptability intervals again after SNG correction. Lower values for steam electrolysis based plant are related to SNG composition, less rich in CH₄ and with a higher mole fraction of nitrogen, which is an inert and gives no contribution to the heating value.

### 4.4. Thermal integration

In Tables 7 and 8 mass and energy streams to be thermally integrated in a heat exchanger network (HEN) able to minimize the requirement of external heat are provided.

Electrolysis feed demi-water heating has been divided into three processes (corresponding to economization, evaporation and superheating steps) because of the different specific heat ratio taken by the stream. A similar consideration holds for syngas cooling after the last methanator, with water condensation taking place in a heat-exchanger section separated from the previous one with gas phase only. "Condensing" indicates the syngas cooling with water condensation before separation. SNG post-cooling is performed before pumping natural gas into the pipeline.

In Figs. 10 and 11 composite curves for hot and cold streams are presented. The curves were built by evaluating the enthalpy.
balance for each temperature interval. Boundaries of interval are defined by extreme temperatures of process involved (see Tables 7 and 8). If hot and cold composite curve are overlaid, it means that in a certain zone of the system cold fluid temperature is higher than hot fluid (i.e., there is thermodynamic inconsistency). Thus, cold composite curve must be right shifted until the minimum difference between hot and cold curves is equal to $\Delta T_{\text{min}}$ defined before. According to composite curves construction methodology [61], three zones should be highlighted.

- “Pinch point”, in which minimum temperature difference between hot and cold fluids occurs.
- External heat requirements, represented by the difference between hot and cold composite curves in the right side of the chart.
- Waste heat represented by the difference between hot and cold composite curves in the left side of the chart.

In both figures, a “plateau” appears, corresponding to the evaporation of reactant pressurized water. “Pinch” occurs at evaporation beginning, i.e., when water is at saturated liquid condition.

As said before, negative values for heat cascades are unacceptable, and they occur for both plants. So, in these systems an external energy input is necessary. This conclusion could be guessed also considering that the highest temperature of a cold fluid coincides with that of a hot fluid (850°C). Since $\Delta T_{\text{min}}$ is not equal to 0, it is impossible to realize a complete heat exchange without external source. Results show also that $T_{\text{op}} = 249.1^\circ\text{C}$.

In Table 9 the most relevant pinch analysis results are summarized. Shown values suggest some observation. At first, the minimum temperature difference is not properly a result, indeed it has been fixed to start the analysis. Pinch temperatures are equal in the two cases because minimum temperature difference occurs at the beginning of water evaporation for both plants. Generally speaking, co-electrolysis based plant shows a better integration because of a lower external heat input and a lower quantity of heat (usually at low temperature) that must be rejected. In particular, a lower external heat requirement will be advantageous from the plant efficiency standpoint.

For both systems, thermal integration plays a key role in the performance optimization. Considering hot fluids for both systems, it results that without thermal integration the external heat requirement would be 4241 kW and 3368 kW for steam and methanation, respectively.
co-electrolysis, respectively. These values are obtained by summing cold fluid thermal powers in Tables 7 and 8.

4.5. Plants energy performance

The overall plant efficiency is calculated as the ratio between the chemical power associated with SNG produced and total electric power input. The total electrical power input includes electricity fed to the SOEC for electrochemical dissociation of reactant feeds to yield syngas; electricity for reactant pre-heating (note that the thermal integration step was necessary to evaluate the amount of external required); AC–DC conversion power losses (the SOEC stack run on DC current, whereas AC current is usually available from the grid); power to drive pump and compressors. The overall plant efficiency can be thus expressed as follows:

\[
\eta = \frac{\text{Power}_{\text{SNG}}}{\text{We}_{\text{TOT}}} = \frac{\text{LHV}_{\text{SNG}} \cdot G_{\text{SNG}}}{\text{We}_{\text{TOT}}} \tag{32}
\]

The LHV of SNG was calculated considering its composition after N₂ blending to comply with quality requirements to feed in the NG grid. Both methane and hydrogen species were considered as fuels (unlike what done for pipeline prescriptions).

In Table 10 some key results useful for plant efficiency estimation are presented. Notably, the energy efficiency of the co-electrolysis plant outperforms that of steam electrolysis case by more than 5 percentage points. Note that DC input item includes the electric power required fed to the SOEC (10 MWe) and the external electricity to pre-heat reactants at high temperature upstream of the SOEC stack. Carbon dioxide compression takes place in a single step without intercooling because this increases overall plant efficiency. If intercooled compression reduces the compression work, without intercooling the outlet temperature from compression stage is higher and is above the pinch point (around 420 °C, as seen). Thus, the heat cascade at the pinch is less negative, i.e., the external heat requirement is lower. The advantage of a lower thermal need is greater than the disadvantage caused by a higher compression work. Then, it has been chosen to avoid intercooling. The item ‘other compression duties’ includes water pumping, nitrogen compression and SNG compression up to 60 bar.

As said, AC total input takes into account also the AC/DC conversion, which regards only DC input and not compression devices drive. It results that AC input is almost equal for both plants, because the higher DC input for steam electrolysis is offset by a lower CO₂ compression work.

The main resulting difference between the two systems is in SNG chemical power, due to the higher LHV for co-electrolysis based plant. This last aspect is related to a higher methane concentration in the final product (i.e., the SNG pumped into the pipeline), and also to a greater SNG mass flow rate. Notably, inter-stack exothermic methanation implies a reduced thermal-neutral voltage that allows for a greater total faradic current once the total DC electricity input is fixed. The Faradic current is indeed related to the molar flow rate of syngas produced through the Faraday’s law. Hence, co-electrolysis is characterized by a greater methane flow rate (7% more than in electrolysis plant) in the outlet SNG that is directly responsible of an overall ‘power-to-gas’ efficiency higher by ~7% (relative increment). In particular, mass flow rate and LHV are characterized by an increase of 5.3% and 1.7%, respectively in co-electrolysis plant. For this reason a higher overall plant efficiency results for the co-electrolysis based system.

The energy requirement (in terms of kW hel/kgSNG) for the two analyzed systems is compared with the performance of the above-mentioned 6 MW Audi e-gas plant, based on alkaline electrolyser technology. For this system an efficiency of 70% (on HHV basis) is reported [50]. Assuming an SNG final composition equal to the SOEC steam electrolysis based system, an energy requirement of 21.0 kW hel/kgSNG has been calculated. This value is higher than the two obtained for the SOEC based systems considered in this work (17.3 and 16.5 kW hel/kgSNG for steam and co-electrolysis respectively), meaning the high-T electrolysis systems potentially yields a lower energy requirement to produce the same amount of SNG than integrated low-T electrolysis methanation processes.

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5. Discussion

Three operating conditions are possible for SOEC: thermoneutral (\(V_{op} = V_{in}\)), sub-thermoneutral (\(V_{op} < V_{in}\)) and over-thermoneutral (\(V_{op} > V_{in}\)) operation. The last operating condition is analysed in more detail in what following.

As seen previously, both analyzed system configurations require an external energy input. It was supposed that this energy is provided by electric heaters, given that heat sources at temperature higher than that of electrolysis are not available within the plant. Assuming this hypothesis, it is possible to identify the global electric requirement, formed by the “duty” to ensure isothermal electrolysis plus the external energy requirement (\(\phi_{ex}\)) to satisfy fluids temperature target. This electric power could be actually

\[
\eta = \frac{\text{Power}_{\text{SNG}}}{\text{We}_{\text{TOT}}} = \frac{\text{LHV}_{\text{SNG}} \cdot G_{\text{SNG}}}{\text{We}_{\text{TOT}}} \tag{32}
\]

The LHV of SNG was calculated considering its composition after N₂ blending to comply with quality requirements to feed in the NG grid. Both methane and hydrogen species were considered as fuels (unlike what done for pipeline prescriptions).
provided whole or partly through the electrochemical device (i.e., the stack). The remaining part will be eventually supplied using electric heaters.

Considering the extreme case in which the power is entirely given by the stack, the third operating condition must be considered \((V_{\text{op}} < V_{\text{m}})\). A threshold voltage can be identified. This value \((V_{\text{lim}})\) is calculated by replacing \(\varphi_{\text{th}}\) in Eq. (22), remembering that it is negative because, from the cell standpoint, is a rejected heat flow rate. Operating at this calculated voltage, the generated heat rate in Eq. (9) is higher than the reaction heat, but it has been assumed that the surplus heat is available to ensure a complete reactant heating. Voltages greater than \(V_{\text{lim}}\) are not suitable, because the net heat flux would be too high. As a consequence, this heat flux would be partly wasted, lowering plant efficiency. Then, SOEC might operate at a polarization above the thermoneutral condition in order to provide an internally arranged final pre-heating stage to reactants. In a real plant exceeding net heat can be used also to compensate for heat losses within the stack, but this last term has been neglected, assuming a good insulating enclosure.

When SOEC works at “sub-thermoneutral” condition \((V_{\text{op}} < V_{\text{m}})\) generated heat is not sufficient to compensate for reaction heat. Then an electric heating device is required not only for external energy supply, but also to ensure thermoelectrolysis. This situation may happen when the thermoneutral current density is considered too high and could represent a risk for cells stability and durability. As an example 1 A/cm\(^2\) is reported [66] as a value implying durability challenges. Thus, operating voltage (if comprised between \(V_{\text{m}}\) and \(V_{\text{lim}}\)) does not affect the electrical input, i.e., the overall plant efficiency. Indeed SNG chemical power is unchanged, because reactant mole flow, \(RU\) and chemical equilibrium issues are the same. Also faradic current is not affected by operating conditions. Until \(V_{\text{lim}}\), operating voltage has impact only on current density and then on active area, according to Eqs. (8) and (20). Rising voltage implies a growth of current density and then a lowering of active area.

At the anode side, pure oxygen production was assumed. Challenges related to oxygen hazard at high temperature are sometimes highlighted in literature [23]. Also, in some studies the use of a sweep gas (usually air, steam or syngas) at anode side has been modeled [39,45]. This would mean to re-consider evaluation of plant efficiency, because the sweep agent must be heated up to cell temperature and also compressed to the same operating pressure. Hence, the mentioned advantages for stack pressurization could be partly or even mostly offset by the need for sweep gas compression and pre-heating. Furthermore, the use of a sweep agent would influence the stack reversible voltage. The anode outlet stream (pure oxygen in our plants) was included in the thermal integration. Before complete cooling down (after internal thermal integration), it could expand in a gas turbine, allowing for additional electric power production useful to boost plant efficiency. This gas could be profitably involved in a series of industrial uses, in which oxygen would be otherwise produced through expensive processes, such as air separation.

Especially for co-electrolysis, a 1D/2D CFD model could be useful in order to better understand the profile of some key parameter (e.g., temperature and gas composition) along the cell. For example, in-cell methanation does not take place evenly along the flow path, but rather when hydrogen concentration becomes higher along the cell. Considering that methanation is an exothermal reaction, this would mean a variable temperature along the cell, causing challenges on thermal management.

Finally, the dynamic behavior and thus capability of storage systems is probably a fact as equally important, if not even more important, than capacity per se. In this sense, the transient response of high-temperature electrolysis systems to load changes must be verified, as well as durability issues associated with load/thermal cycling of the stack materials.

6. Conclusions

Two different plants for the production of SNG via high temperature electrolysis and catalytic methanation have been designed and modeled. In the steam electrolysis—only plant, hydrogen production takes place, with subsequent \(\text{CO}_2\) injection before methanation. In the other plant analyzed, \(\text{CO}_2\) is also key reactant together with \(\text{H}_2\) in high-temperature co-electrolysis of steam and carbon dioxide. Notably, methane formation already during co-electrolysis is thermodynamic conditions is favourable and \(\text{Ni}\) in the cathode electrode is kinetically fast to sustain methanation reactions.

With the co-electrolysis based plant a higher overall efficiency was achieved (81.4\% against 76.0\% for steam electrolysis), due to the larger methane content into the produced SNG (meaning a greater LHV) and to the higher SNG mass flow rate.

Sensitivity analyses were used to evaluate the opportunity of cell pressurization. From the electric consumption standpoint pressurization seems to be advantageous in order to increase the overall plant efficiency. But from an economic point of view, this positive aspect could be offset by an increased cost of some components (such as vessels, heat exchangers, enclosures, etc.). Moreover, for co-electrolysis high cell pressure implies lower thermoneutral current density, i.e., higher active area (assuming a fixed value for faradic current).

A nearly perfectly matching thermal integration between the SOEC plant (whose reactants need to be heated up to 850 °C in case of thermoneutral operation) and the exothermic methanation section allows to minimize the external heat requirement of both plants. In fact, both integrated processess are characterized by an external input around 160 kW each against an overall required thermal input of 3 and 4 MWh for steam electrolysis and co-electrolysis, respectively.

References
