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Investigation of off-design characteristics of solid oxide electrolyser (SOE) operated in endothermic conditions

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Abstract. One of the key issues in the energy production sector worldwide is the efficient way to storage energy. Currently, more and more attention is focused on Power-to-Gas (P2G) installations, where excess electric power from the grid or various renewable energy sources is used to produce different kind of fuels, such as hydrogen. In such cases, generated fuels are treated as energy carriers which, in contrast to electricity, can be easily stored and transported. Currently, high temperature electrolysers, based on solid oxide cells (SOC), are treated as an interesting alternative for P2G systems. Solid oxide electrolysers (SOE) are characterized as highly efficient (~90%) and long-term stable technologies, which can be coupled with stationary power plants. In the current work, the solid oxide cell stack was operated in electrolysis mode in the endothermic conditions. Based on the gathered experimental data, the numerical model of the SOC stack was created and validated. The prepared and calibrated model was used for generation of stack performance maps for different operating conditions. The results allowed to determine optimal working conditions for the tested stack in the electrolysis mode, thus reducing potential costs of expensive experimental analysis and test campaigns.

1 Introduction

Currently more attention in power and energy sector is focused on minimizing the wide usage of fossil fuels, mainly due to their negative impact on the environment. At the same time, various solutions concerning power generation and efficient ways to store energy are correlated with renewable energy sources (RES). The most commonly used technologies world-wide are solar and wind based power systems. The main issue with these solutions is dependence on local weather conditions, thus such energy sources are intermittent, which in many cases might be highly undesirable [1-3]. In response to that, many scientific and R&D entities are analysing different counter-solutions. Many specialists treat hydrogen as the gas of the future, which can be used as one of the main substrates in creating different and more calorific fuels, or directly convert it as the main power source for production of energy. These technologies are highly suggested for application in systems aiming to minimize pollution emissions to the atmosphere.

At present, steam reforming is the most commonly used method to generate hydrogen [4,5], which is not a preferable solution in long-term perspective. As a result, in recent years new methods for efficient and clean hydrogen production are developed [6,7]. Steam electrolysis is currently considered as a preferable technology for application in mid- and large-scale

hydrogen production installations, due to its high efficiency [8-10]. Among the existing electrolysers, commercially available and most advanced are alkaline and proton exchange membranes (PEM), which are used for low temperature electrolysis processes [11]. In recent years however, high temperature steam electrolysis based on solid oxide cells (SOC) proves to be a much better solution, due to lack of expensive catalysts and high hydrogen generation efficiency (~90%) [12,13]. The comparison of performance between electrolysis technologies is presented in Fig. 1, showing polarization areas for specific devices.

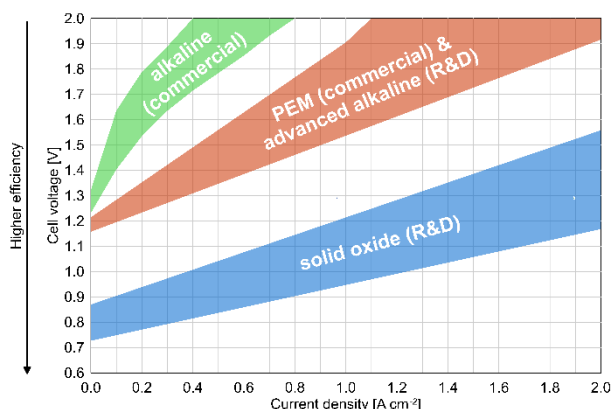


Fig. 1. State-of-the-art steam electrolysers (based on [13]).

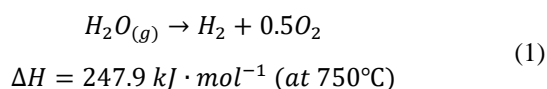
The performance of the electrolyzers can be evaluated by comparing the need of electric power for the electrolysis reaction, generating the same amount of hydrogen. The operating areas presented in Fig. 1 show that high temperature electrolyzers, based on solid oxide cells, require less power than low temperature technologies, thus their hydrogen production efficiency is higher. The difference is caused mainly by higher internal resistances between low- and high-temperature cells, hence the usage of the second technology might be more economically profitable in long-term perspective.

Solid oxide cells can operate as fuel cell which generates heat electric power or as an electrolyser for production of clean hydrogen and oxygen, when the specific conditions are met. Additionally, one of the main advantage of SOC-based technologies is the possibility to simply integrate them with existing stationary systems, either dedicated for production of electric power and heat or hydrogen [14].

Efficient way for storage of energy is currently an important and urgent topic in power sector world-wide. For that reason, more attention is dedicated for solutions that allows to both generate and distribute energy with minimization of potential losses. In such cases, electrolyzers proves to be a preferable option, where generated hydrogen, treated as energy carrier, can be stored and transported for long distances. Systems with such topology are known as Power-to-Gas (P2G) installations where, besides hydrogen, methane and other, more calorific gases might be generated [15]. This concept can be further expanded by implementing proper chemical reactors, thus allowing to produce various liquid fuels (Power-to-Liquid (P2L)).

2 High temperatures electrolysis

Water electrolysis reaction was discovered at the end of XIX century [16], but is still used in modern technologies, such as in high temperature solid oxide electrolyzers (SOE). The operating temperature of SOE cells is from 600°C to 1000°C, which is the result of used materials, such as ZrO₂, for the electrolyte layer [14]. The steam electrolysis reaction is presented in Eq. 1:



where, ΔH is the reaction enthalpy. Operation of solid oxide electrolyzers is shown in Fig 2.

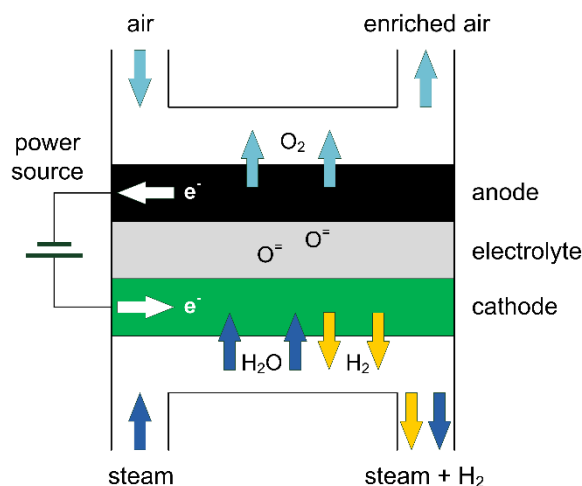


Fig. 2. SOE cell working principle.

Solid oxide cell consists of three different layers: cathode, anode and electrolyte. For the electrolysis operation, steam and electric power are delivered to the porous, fuel electrode. This results in reduction of water molecules for oxygen ions (O²⁻) and hydrogen in the cathode. Oxidant electrode is usually supplied with air but different gases might also be delivered or vacuum conditions might be applied, depending on the wanted SOE operation. In every case, oxidant molecules are formed on the anode side. The electrolyte is a thin layer which allows to pass only oxygen ions. Its structure has to be properly prepared in order to block diffusion of hydrogen and other, potential gases [17].

The SOE stack can operate in three different operating modes: thermo-neutral, endothermic and exothermic, which are strictly correlated with temperature and applied current [18,19]. During the electrolyser operation, part of electric power is used in the steam electrolysis reaction, while the rest is lost in form of the heat. As a result, temperature distribution in the stack depends on the compromise between the energy consumed by the reaction and the generated heat. When the amount of heat caused by the electric power exceed the required heat for the electrolysis reaction, the stack operates in the exothermic conditions, thus in-stack temperature rises. For the endothermic conditions, electrochemical reactions uses more heat than is delivered to the stack via electric current, thus lowering the stack operating temperature. In such case, additional heat needs to be delivered to the stack [20]. The switching point between exothermic and endothermic operation mode is known as the thermo-neutral voltage. Its value is dependent on the stack operating temperature and type of the electrolysis reaction, such as steam electrolysis, carbon dioxide electrolysis or mixed. Thermo-neutral voltage is calculated via Eq. 2, which is based on the Faraday's Law:

$$E_{th} = \frac{\Delta H}{n \cdot F} \quad (2)$$

where, ΔH is the reaction enthalpy, F is Faraday's constant and n is the number of electrons needed in the reaction. For the steam electrolysis at 800°C , the thermo-neutral voltage is 1.28V .

Depending on the power system configuration with the installed SOE electrolyser, different operating modes are more preferable [21]. The main disadvantage of endothermal operation is need to deliver both heat and electricity for the electrolysis reaction. However, this can be compensated in case, where the SOE stack is connected to the external heat source. For the exothermal state, more electric current must be applied to the stack, which might result in damaging the cells in long-term operation. In the previous studies it was observed that for high currents in the electrolysis mode, the delamination of the oxidant electrode from the electrolyte layer might occur. In this process, interface of anode-electrolyte suffers build up of oxygen partial pressure, resulting in irreversible damage on the cell [22-24]. At the same time, high current affects the nickel-based cathode, which might suffer more rapid degradation [25-27]. As a result, stable and long-term operation of SOE-based systems, which is the aim for potential commercialization of the technology, is more difficult to achieve in exothermal state. For that reason, working in endothermal or near thermo-neutral conditions are more preferable.

In the current study, the numerical model of solid oxide electrolysis stack was designed and compared with gathered experimental data during endothermal operation of physical device. Next, the tuned model was used to generate stack performance maps for different operating conditions. The results allowed to determine optimal working conditions for the tested stack in the electrolysis mode, thus reducing potential costs of expensive test campaigns.

3 Methodology

The solid oxide electrolysis technology is under research and development for more than 40 years, but there are not many publications related to modelling of their operation both in stationary and transient cases. Most of the SOE numerical tools are based SOFC mathematical methodologies, due to comparable mechanisms, such as gas diffusion and similar electrochemical behaviour. The proper SOFC modelling approach can be modified in order to simulate SOE operation [28-30].

In the chosen methodology for the present study, solid oxide cells electrical operation is calculated as equivalent electric circuit. This solution was already used to predict performance of SOFC-based power units both in steady state [31] and in transient operations [32]. In both cases, proposed methodology was validated and calibrated based on the experimental data, resulting in prediction error below 5%. This concept was currently adopted for simulation of solid oxide electrolyser. The electric circuit equivalent of SOE is shown in Fig. 3.

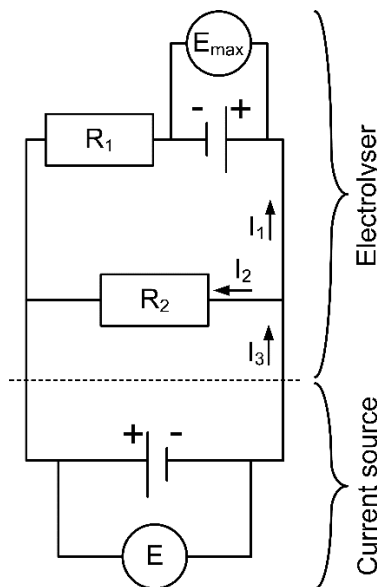


Fig. 3. Electric circuit equivalent of SOE.

In the proposed diagram, representing electrochemical cell operation, current delivered from the power source to the SOE is shown as I_3 . Next, it is divided into flow of electrons used in the electrochemical reaction (I_1) and I_2 which represents the total electronic conductivity.

In this approach, the voltage of the single cell is calculated by solving the electric circuit based on Ohm's and Kirchhoff's Laws :

$$E_{cell} = \frac{E_{max} + i_{max}r_1\eta_s}{\frac{r_1}{r_2}(1 - \eta_s) + 1} \quad (3)$$

where, E_{max} is the highest possible voltage obtained during isothermal process; η_s is the steam utilization factor, which is defined by the current working conditions of the cell; i_{max} is the maximum current density correlated with amount of steam delivered to the cells; r_1 is the area specific internal ionic resistance representing oxygen ions permeability through the electrolyte and r_2 is the area specific internal electronic resistance which corresponds to solid electrolyte electric conductance. The full description of the used methodology is presented elsewhere [33].

In the current analysis, selected SOE module consists of two separated stacks, 30 cells each, as shown in Fig 4.

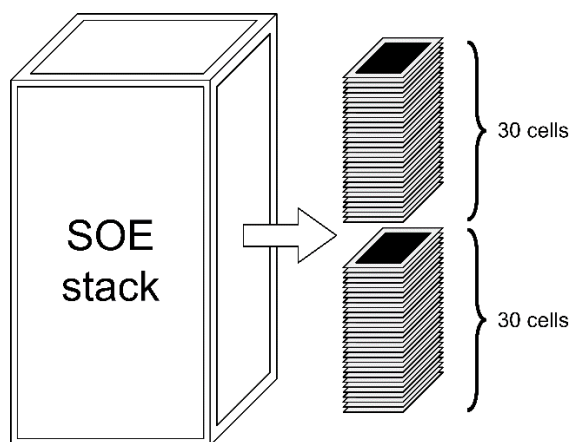


Fig. 4. SOE module concept.

The single stack contains 30 cells, where the cathode is porous NiO/GDC, the electrolyte is dense 3YSZ and the anode is double layered 8YSZ/LSM–LSM. The active area of a single cell is 128 cm². The chosen modeling approach includes technical specification of the stack, such as physical properties of the used materials for cells and interconnectors, thus minimizing the usage of empirical and semi-empirical constants and equations.

The model of the SOE stack was designed and implemented in Aspen Hysys modeling software. In order to properly simulate operating in the electrolysis mode, the proposed numerical tool was enhanced with additional in-house codes, which were determined based on the performed experiments with single cells and fully-dimensional stack.

4 Results

The numerical model of the stack has undergone a validation process, based on the data gathered during measurements on the SOE module with two 30-cell stacks connected electrically in series. The experiments were performed in the electrolysis mode, operating mainly in the endothermic conditions.

The polarization curve of the SOE module was generated in constant 750°C. In order to maintain stable temperature during measurements, proper power of inlet air heaters was set for each saved point. The validation of the proposed model is shown in Fig. 5.

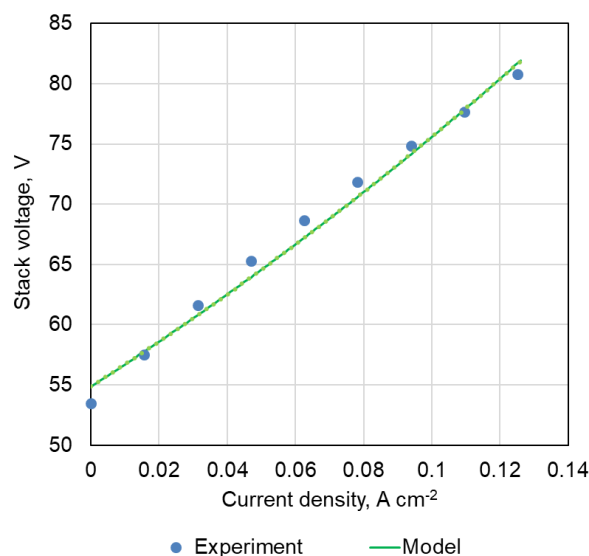


Fig. 5. Model validation

The average prediction error was less than 1.41%, where the relative prediction error did not exceed 3%. While operating in the electrolysis mode, inlet gas for the cathode was composed of steam and additionally hydrogen and nitrogen, in order to maintain reductive atmosphere on the Nickel-based part of the cell. For the anode side, air was used as the oxidant.

Based on the known parameters and technical limitation of the stack, the validated model was used to generate performance maps of the SOE module. Such approach allows to determine optimal operating conditions for the stack, without having to realize expensive and time-consuming experimental campaigns. The main limiting factor included in the simulations is the maximum steam utilisation factor (SU), which shows the molar amount of steam used in water electrolysis reaction. There is no strict limiting value concerning SU reported in the available literature, but it is commonly assumed that 80% is the highest value [37].

In the realized numerical activities, two performance maps were generated for different input parameters: stack power and stack voltage. The amount of air and mixture of hydrogen and nitrogen were constant for every case. Due to the fact, that experimental analysis of the stack were performed only at 750°C, the same temperature was used in the simulations. The only variables in the realized simulations were current density and flow of delivered steam. The obtained stack voltages and power are shown in Fig. 6 and 7, respectively.

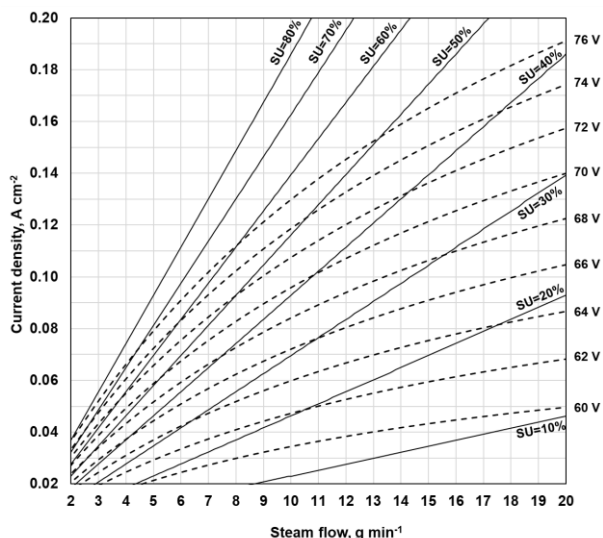


Fig. 6. SOE module performance map: voltage.

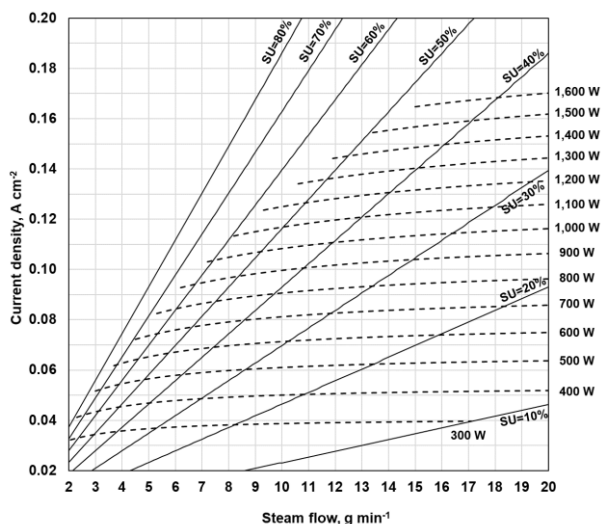


Fig. 7. SOE module performance map: power.

In order to operate in the endothermic conditions, maximal stack voltage was set to 76V, which corresponds to ~1.27V per cell. In Fig. 7, the dashed lines, representing different values of generated power, were presented only in the area which did not exceed 76V. Operating above this conditions, SOE module would work in exothermic mode, generating more heat than required for the electrolysis reaction, but resulting in potentially more rapid degradation of the cells.

5 Conclusions

In the current work, SOE module consisting of two stack with 30 cells each, was modelled and simulated in endothermic conditions. Operation below thermo-neutral point is more preferable solution compared to exothermic states, due to extended long-term durability of the stack and lower risks for degradation and potential damages in the cells. Based on the generated performance maps of the SOE module, it is possible to determine preferable operating conditions, depending on the wanted results. This allowed to perform simulations for different steam flows and current densities, without

the need to realize expensive and long experimental campaigns. For the current study, SOE module was tested only in 750°C. Further work in this topic will be dedicated in performing additional tests with the presented stacks in different operating temperatures. Obtained data will be used to further tune the proposed numerical model and generate additional performance maps, thus allowing to determine SOE module behaviour in wider operational range.

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