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Operating results of PEMEL, AEL and SOEC systems

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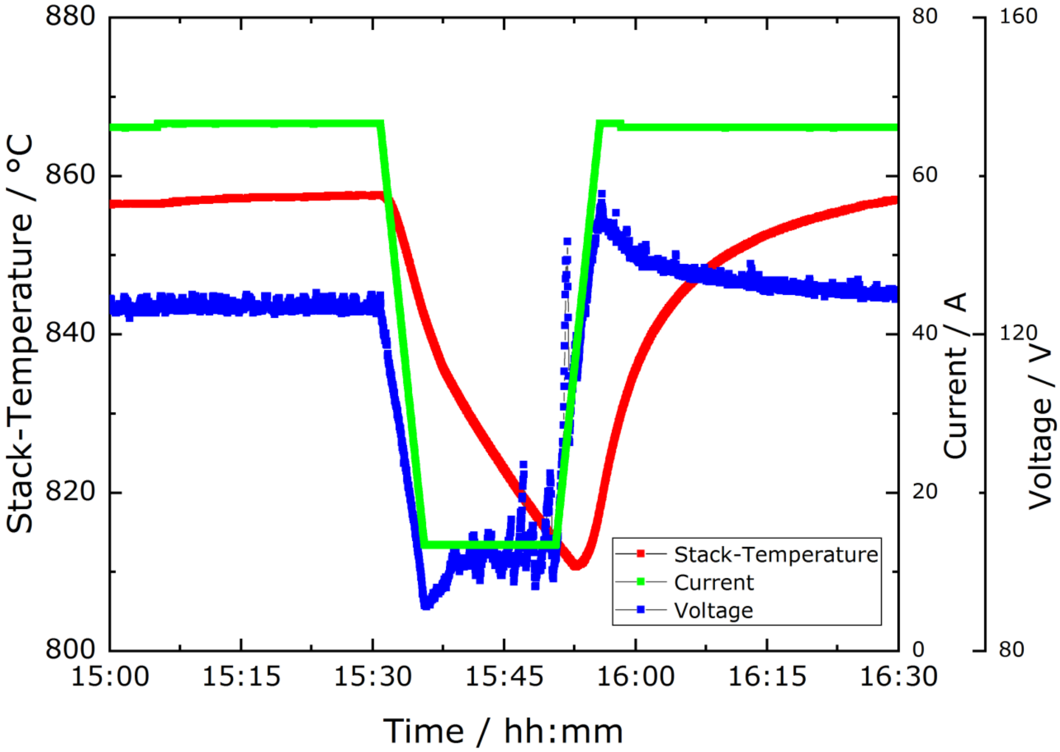
Abstract

Three commercially available stand-alone electrolyser systems are tested, covering the significant technologies alkaline water electrolysis, proton exchange membrane water electrolysis and high temperature steam electrolysis using solid oxide electrolysis cells. The hydrogen outputs of the systems are in the range between 5 to 10 $Nm^3 h^{-1}$ hydrogen at delivery pressures between 10 and 35 bar. Each system comprises its own water purification, hydrogen purification, cooling units and safety systems.

Goal of the comparative study is to evaluate the systems regarding reaction time, stack stability, durability of Balance of Plant and maintenance effort under dynamic operation and grid supporting operation. Therefore different load profiles have been defined, simulating the shift between stationary and dynamic application. In this paper the results of the on-going test procedure up to this date are presented and discussed.



The diagram shows the behaviour of the temperature, cell voltage and current during a load change from 100% to 25% of the SOEC system.

Introduction

In the Carbon2Chem project (03EK3038B), funded by the German Federal Ministry of Education and Research (BMBF), possible large energy-related applications processing exhaust gases from steel production to chemical raw materials are investigated [1]. The conversion uses the majority of the carbon dioxide within the steel mill exhaust gases and needs additional hydrogen that will be supplied by electrolysis. To reduce the carbon footprint of the process, the production of “green” hydrogen on the basis of regenerative energy sources is of significant importance. Additionally the supply of “green” hydrogen contributes to the transition from fossil to renewable energy sources as well as advances “carbon to chemicals” and “power to gas” applications [2]. For the production of “green” hydrogen, a dynamic operation of an electrolyser must be possible to operate according to the supply of regenerative energy and the regulations of the electrical grid. Furthermore, the influence of the dynamic operation on the electrolyser itself has to be investigated.

1. Scientific Approach

Today, three different electrolysis technologies are mainly applied to produce “green” hydrogen from water and renewable electric energy. These are Alkaline Water Electrolysis (AEL), Proton Exchange Membrane Water Electrolysis (PEMEL) and High Temperature Steam Electrolysis based on Solid Oxide Electrolysis Cells (HTSE or SOEC).

The most mature of these three technologies is the AEL. Systems with a power of hundreds of MW and thousands of $Nm^3\ h^{-1}$ production rate are already installed today [3].
The AEL operates at temperatures of about 50-80 °C using caustic aqueous KOH or NaOH with a concentration of 20-30 wt.% as electrolyte. In AEL the adjacent bipolar cells are connected while a diaphragm separates the electrodes of each cell [3]. At the cathode water is reduced to hydrogen and hydroxide. The latter passes the diaphragm and reacts to oxygen and water at the anode. As the environment is highly caustic, the components of the electrolyser need to have a high corrosion resistance. Therefore, mainly Ni-based alloys are used as electrode catalysts (e.g. Ni/Co/Fe as an anode catalyst and Ni/Co as a cathode catalyst), as porous transport layers and for the parts in contact with the electrolyte [4].

In PEMEL a proton conductive solid polymer membrane is used instead of a diaphragm. This offers the advantage of using de-ionized water, as no liquid electrolyte is required, as well as higher current densities up to $3\ A\ cm^{-2}$ or more [5]. The operating temperature compares to the temperature of the AEL technology. The PEMEL is as well constructed in a bipolar design. Water is split at the anode into protons and oxygen. The protons pass through the membrane and react with electrons to hydrogen at the cathode. In most cases the electrolyte membrane is made of a PFSA polymer, which is a super acidic ion exchange resin [5]. The high potential of up to 2.4 V at the anode in combination with the polymer leads to a highly corrosive environment. Hence, only highly corrosion resistant materials and catalysts, e.g. titanium and iridium/oxides can be used in PEMEL.

The HTSE based on SOEC operates in contrast to the both before mentioned electrolysis technologies at temperatures of about 500-950 °C. The water fed to the system is vaporized and split in the cells at voltages of 0.9 to 1.5 V [6]. At the cathode water is reduced to hydrogen and oxide ions. These ions pass the permeable ceramic membrane and react at the anode to oxygen. The downside of the high temperature, which leads to the desired low cell voltages, is a slower reaction to alterations in the operation conditions in comparison to the other two electrolysis technologies. This includes a significant longer start up and shut down procedure. While the HTSE is still under development first products are launched in the market.

ZBT is actively collaborating with the Joint Research Centre (JRC) of the European Commission and the leading institutions on the development of EU harmonized test and durability protocols for water electrolysis systems. Therefore, the experience gained with industry scale water electrolysers in the frame of the Carbon2Chem project will contribute to the development of the EU harmonized protocols in this topic.

2. Experiments/Calculations/Simulations

ZBT investigates the suitability and industrial operational capability of the three electrolysis technologies for dynamic operation. For this purpose, an AEL, a PEMEL and a SOEC system in the hydrogen production range of maximum 5 to 10 $Nm^3 h^{-1}$ were procured and installed in the outside area of ZBT. All units are containerized standalone plants and are equipped with the necessary auxiliary devices like input water purification, cooling device for stacks, drying system for hydrogen quality, air conditioning and ventilation, as well as safety features.

The AEL system produces up to 10 $Nm^3 h^{-1}$ hydrogen at a maximum pressure of about 12 bar. The PEMEL system provides up to 5 $Nm^3 h^{-1}$ hydrogen with a pressure of 35 bar. The HTSE supplies a maximum of 5 $Nm^3 h^{-1}$ hydrogen. The SOEC stacks operate at ambient pressure, but due to an inbuilt pressure swing adsorption the hydrogen can be delivered at a pressure of about 10 bar. In table 1, the main characteristics of the three electrolysis units are listed.

Table 1: Main characteristics of the three electrolysis systems [7]

	AEL	PEMEL	SOEC
Max H_2 production rate [$Nm^3 h^{-1}$]	10	5	5
Output H_2 pressure [bar]	10	35	10 (after PSA)
Operation range of the nominal power [%]	25-100	20-125	20-120
Operating temperature [°C]	60-80	50-70	850-880

Aim of the testing is the investigation of the operation behaviour of the different electrolyser technologies under fluctuating power conditions. Hence, the systems are operated with different load profiles at their maximum output pressure. These load profiles represent the operation at constant current as well as at alternating current values based on various scenarios. In this extended abstract, the former will be referred to as stationary operation, while the latter is called dynamic operation.

The stationary tests were conducted at a production rate of hydrogen of 100%, to investigate the general behaviour and stability of the plant. The results were evaluated, also in the perspective of first signs of degradation of the electrolysis stacks. For the dynamic operation the production rate was increased and decreased within a period of 5 Minutes in reference to the secondary control power of the electrical power grid. In between the ramps, the hydrogen production was kept stable for 15 minutes.

As the PEMEL system was not ready for operation (see results) alternative measurements were realized. Thus, the before mentioned dynamic and stationary operation were carried out only with the AEL and the SOEC system.

Figure 1 depicts the stationary operation of the AEL system in March 2019. The time frame covers 16 days.
The green line represents the current that is applied to both of the 2 stacks of the system. It starts from 0 A and rises to 109.25 A, which equals 100 % of the hydrogen production rate. While the current rises, the corresponding voltages of both stacks increase as well from 0 V to 265 V for stack A (upper blue line) and 266 V for stack B, respectively. Both voltages decrease over the course of the operation to a minimum of 254 V for stack A and to 251 V for stack B. A degradation of the stacks cannot be observed, as the voltages of both stacks decrease over time.

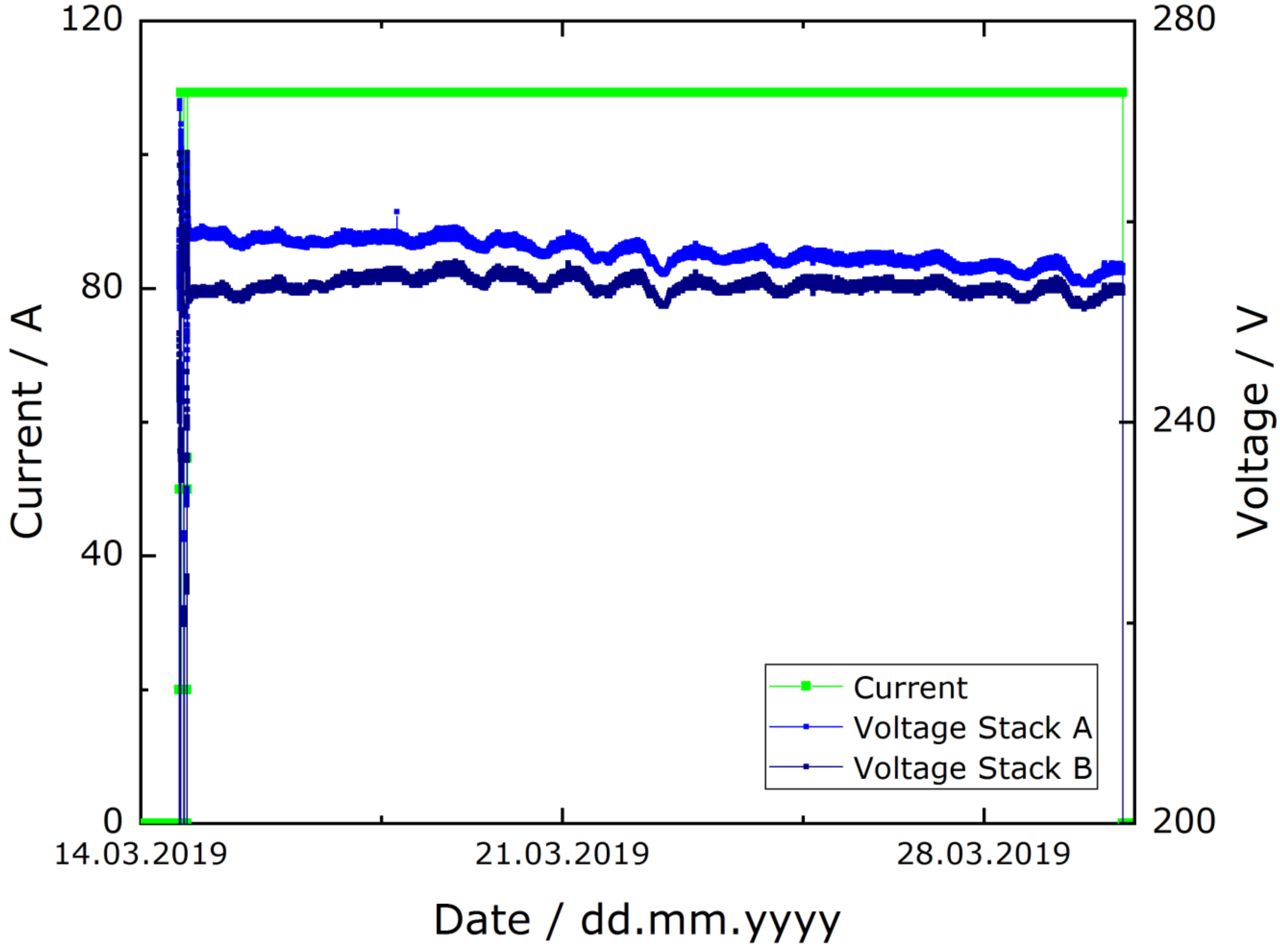


Figure 1: Stationary operation of the AEL

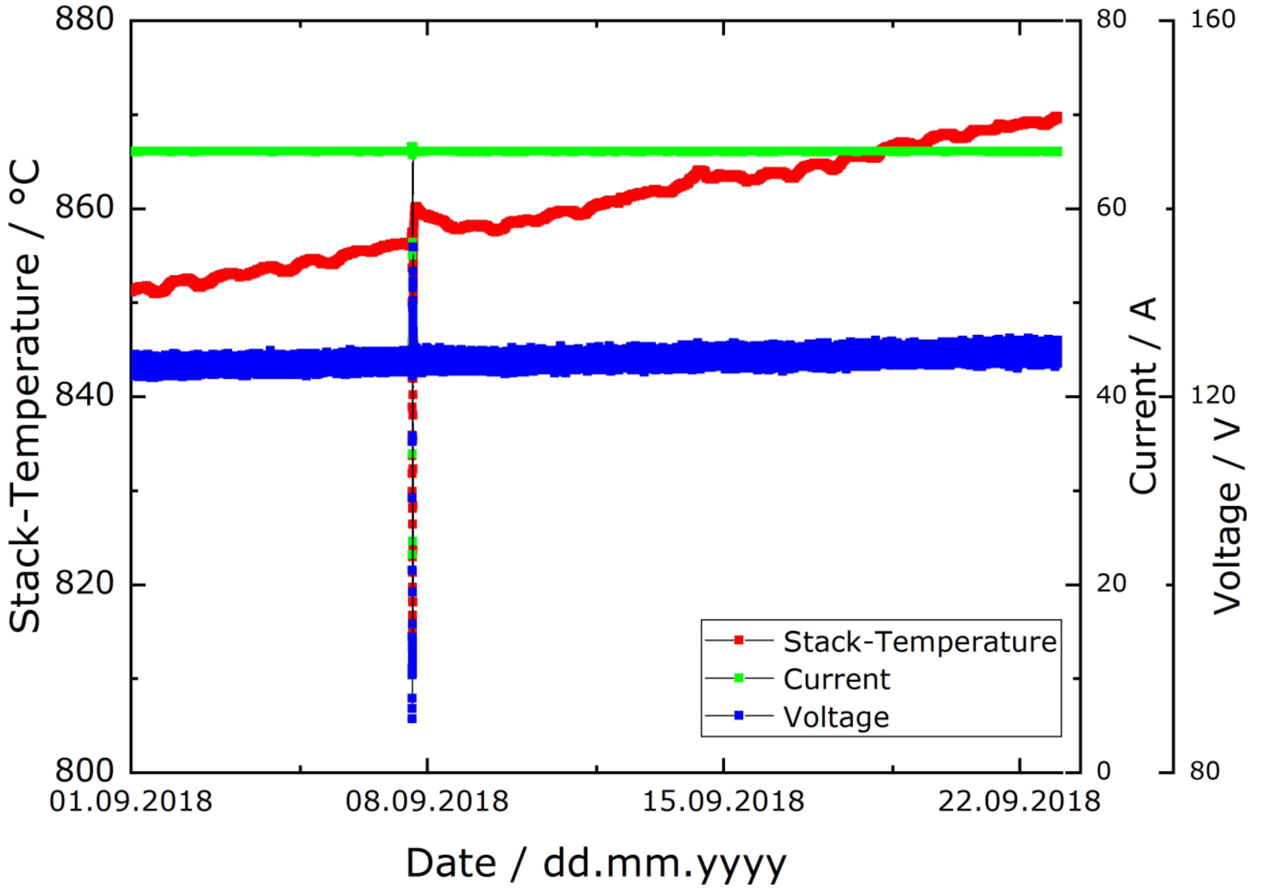


Figure 2: Stationary operation of SOEC

In figure 2, the stationary operation of the SOEC system is presented. The current, voltage and maximum stack-temperature for one of the modules of the plant, which consists out of 3 stacks, are shown. The current (green line) was set to 66.1 A, what corresponds to 100 % of the production rate of hydrogen. Over the course of the operation, the voltage of the module (blue line) rose from 122.7 V to 125 V, while the temperature (red line) increased from 851.1 °C to 870 °C.

As stack-temperature and voltage of an HTSE system can indicate degradation of the system, a quotient can be calculated for both of these factors. For the temperature, the degradation per day results in 0.83 °C/d. The quotient for the voltages is 102 mV/d.

On the 7th of September 2018, an exemplary dynamic profile was applied to the system, which is depicted in figure 2 as well as in figure 4.

Figure 3 shows the dynamic operation of the AEL. The currents of the 2 stacks are drawn in light (stack A) and dark (stack B) green, while the voltages are depicted as light blue (stack A) and dark blue (stack B). Both currents start at 100 % production rate (109.25 A). The hydrogen production rate is continuously lowered to 20 % over the course of 5 Minutes. The currents of the 2 stacks drop to 52 A each, which equals 50 % of the production rate. As the rate goes beneath 50 % and decreases to 20 %, stack A is turned off and the current of stack B rises at first to 96.14 A. The minimum current of 43.7 A is reached at 20% production rate. The minimal production is kept stable for 15 Minutes and raised again over the next 5 Minutes to 100 %. At 50 %, stack A is switched on again, what can be seen as current and voltage of stack B drop.

The voltage of stack A and B develop likewise, starting at 249 V and 247 V, respectively. At minimum production rate and over the course of the ramp up process, the voltages of stack A and B increase above the previously obtained value to 260 V for stack A and 263 V for stack B. At stable production at 100 %, each voltage returns to their initial value.

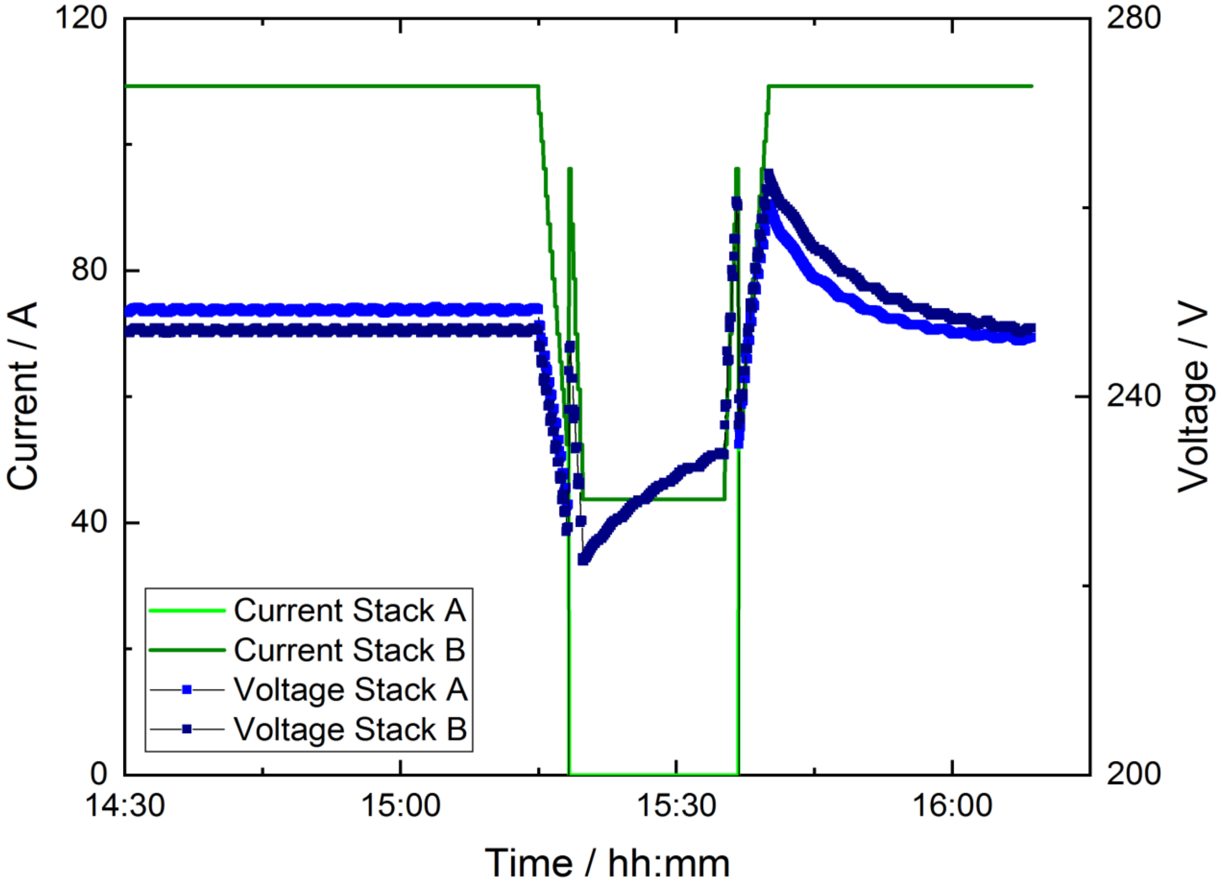


Figure 3: Dynamic operation of the AEL

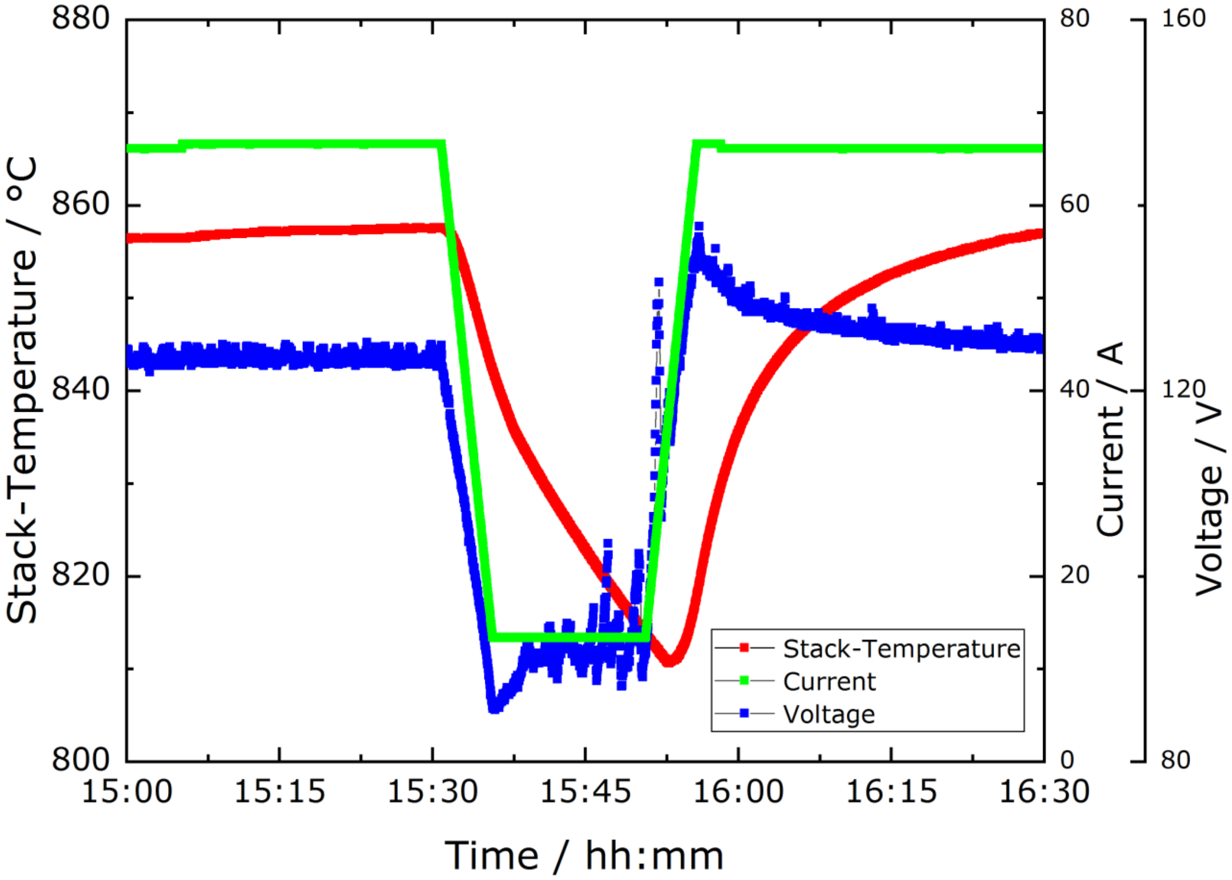


Figure 4: Dynamic operation of the SOEC

Figure 4 presents the dynamic operation of the SOEC. The green graph depicts the current of one module, the blue graph shows the voltage and the red graph the temperature of the stacks. As the current decreases from 66 A to 13.4 A, voltage and temperature drop as well. After 15 minutes at 20 % production, the current increases again. This leads to an imminent rise of the voltage. The graph of the temperature follows this development with several minutes delay. It can be seen that the voltage exceeds the value obtained before the cycle (137 V) but reaches the old value (124 V) after the temperature rises to its original value (859 °C).

As the PEMEL system was not ready for operation alternative measurements were realized using a self-developed PEMEL test bench and commercially available PEMEL short stacks from American and German manufacturers. The test bench allows characterization of short stacks with up to 7 cells and an active area from about 25 cm² up to more than 500 cm². The possible electrical stack power is up to 40 kW with a maximum current of 2000 A. The test bench can be operated with a pressure of up to 35 bar, differential pressure as well as equal pressure on both electrode sides. The water feed can be realized on both sides. The operation is fully automated including an electrochemical impedance spectroscopy performed with a Gamry Reference 3000 AE Potentiostat / Galvanostat.

The following data show preliminary results of a short stack operated with highly dynamic load profiles changing the load from minimum to maximum and back to minimum within 10 seconds for several thousand cycles at different operation temperatures. Goal of this tests is to investigate the degradation of PEMEL stacks for highly dynamic operation on the one hand and on the other to develop in the near future Accelerated Stress Test (AST) protocols together with the industrial and scientific community which is united in the ANNEX 30 activities of the IEA and activities led by the JRC of the European Commission. Figure 5 shows such an experiment with about 8280 load changes for three different temperatures each.

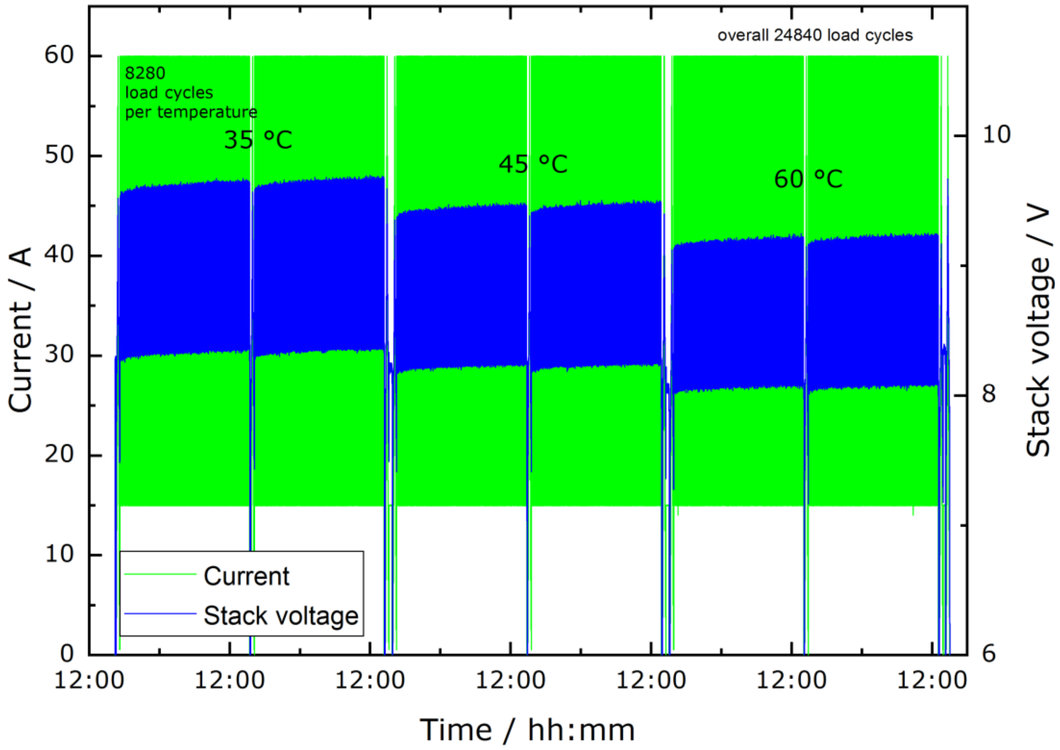


Figure 5: Highly dynamic operation of a PEM stack

The current is cycled between 15 and 60 A which are the minimum and the maximum operating current according to the manufacturer specifications. The temperatures of 35 °C and 45 °C are also within the specifications while the temperature of 60 °C is higher than the manufacturer officially permits. Each temperature block contains three polarization curves and impedance measurements which are performed at the beginning, in the middle and at the end of the load cycling. The whole test ends with a reference measurement (polarization curve plus impedance measurement) at a temperature of 35 °C. As expected the stack voltage decreases with increasing temperature while it increases with operation time. As one can see the degradation is partially reversible. The stack voltage starts at a lower level after interruption of the dynamic operation. Figure 6 shows data from the previous figure but with a more detailed depiction of the stack voltage (right y-axis).

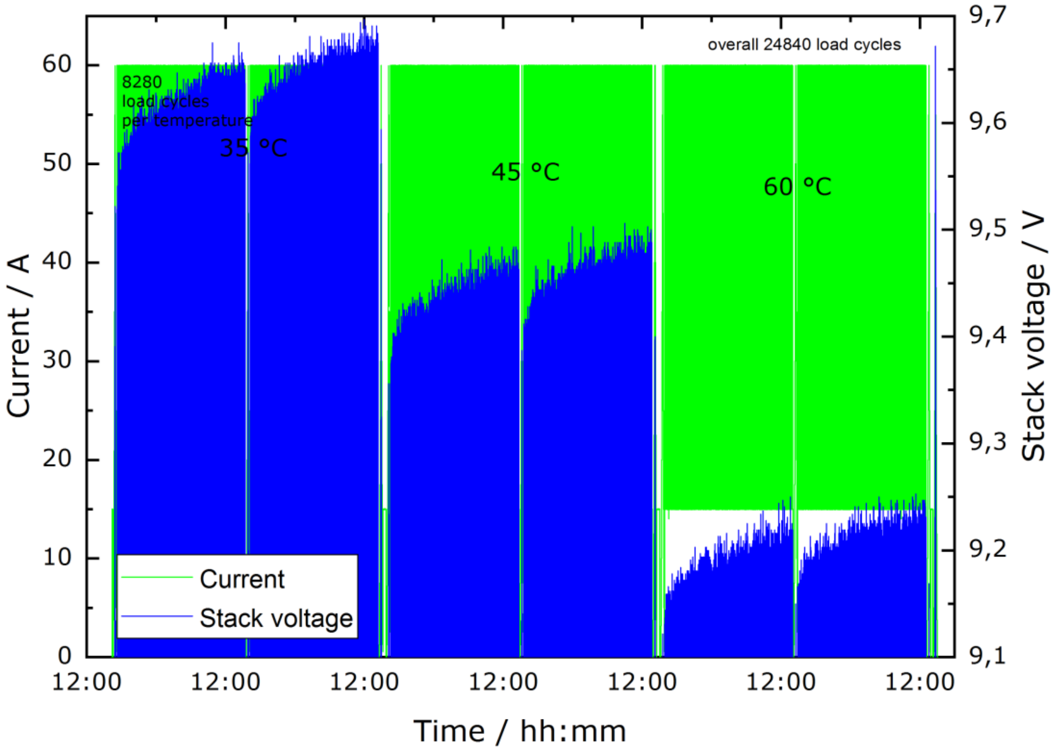


Figure 6: Highly dynamic operation of a PEM stack

Figure 7 shows the polarization curves which were recorded during the dynamic operation as discussed before. In order to determine the non-reversible degradation rate, the stack voltages of the first and the last measured polarization curve (both at a temperature of 35 °C) are compared. The stack voltage at the beginning is about 9.5 V at 60 A. This corresponds to a cell voltage of about 1.9 V. At the end of the test the stack voltage is about 9.64 V, corresponding to a cell voltage of ca. 1.928 V. This results in a degradation of about 28 mV during 140 h of operation. From this a degradation rate of about 200 µV/h can be calculated.

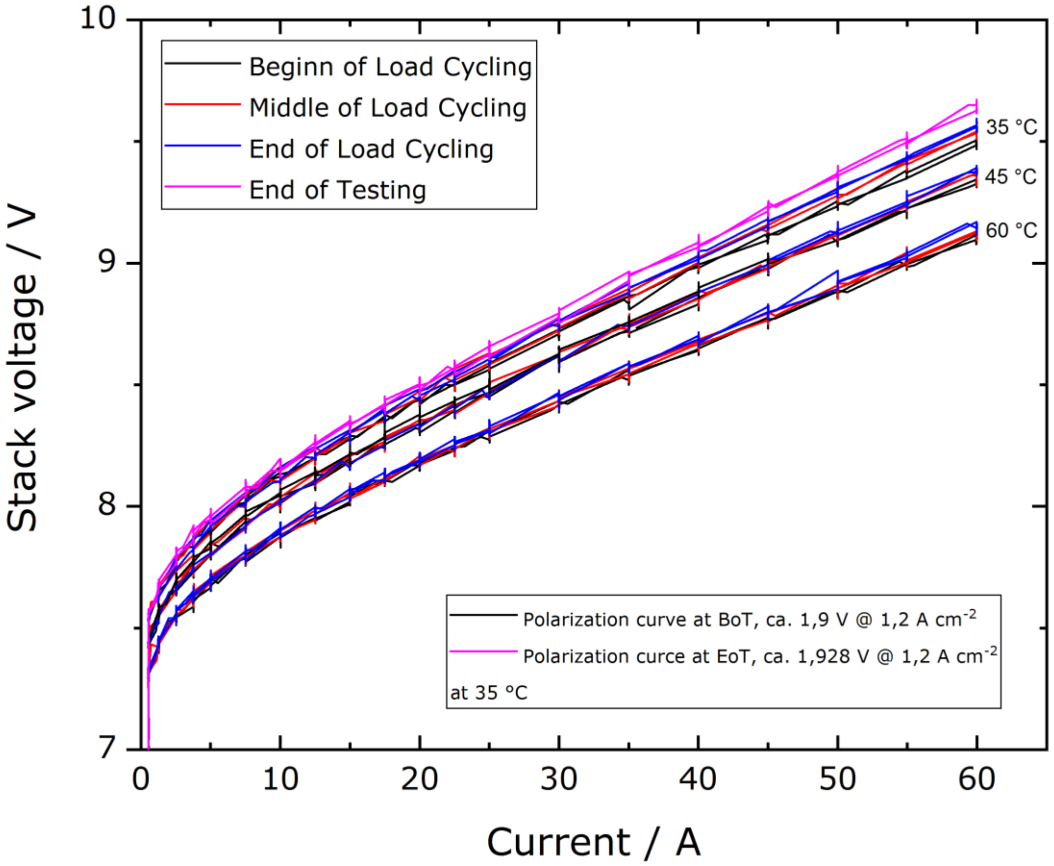


Figure 7: Polarization curve obtained at dynamic operation of a PEM stack at three different operation temperatures

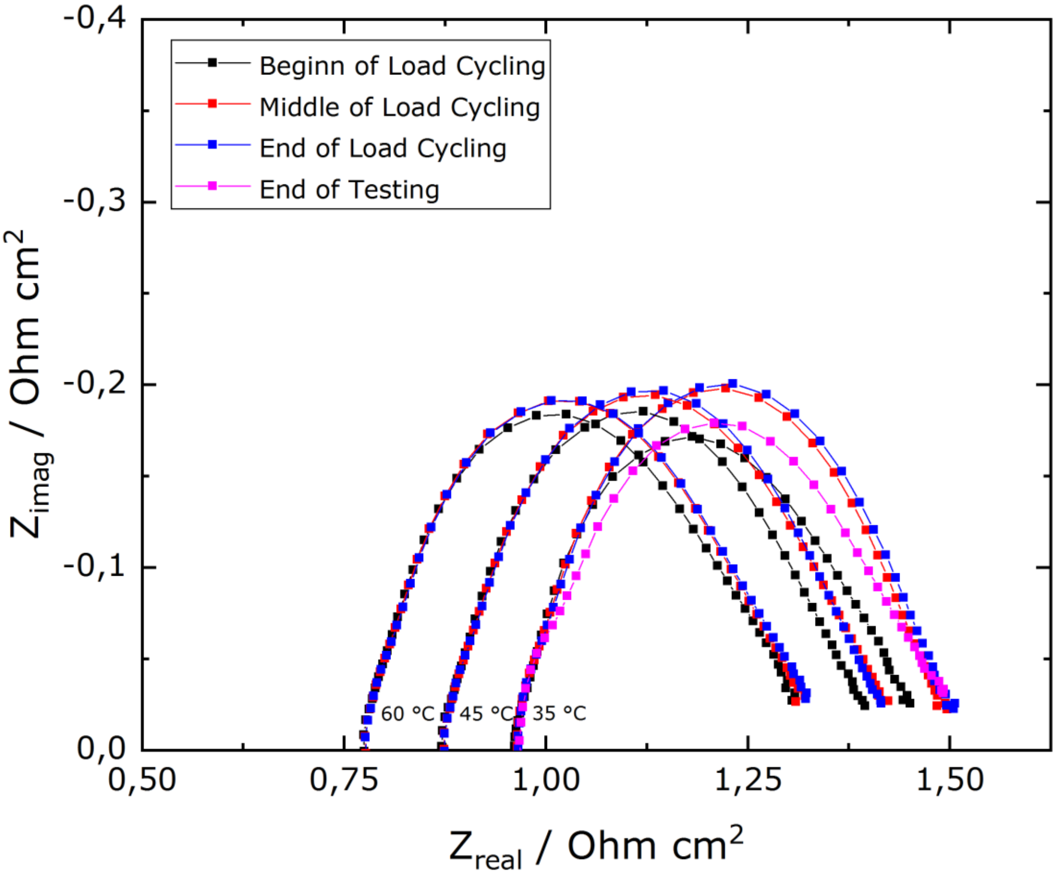


Figure 8: Corresponding Nyquist plots at different temperatures

Additionally, as mentioned before impedance measurements were performed before, in the middle and at the end of load cycling in order to examine the degradation effects. Figure 8 shows the Nyquist plots of these measurements. As expected the impedance decreases with increasing temperature corresponding to the stack voltage. It can be seen that the operation has no impact on the left intercept point of the semi-circle with the x-axes. This means that the ohmic resistance remains stable for each temperature. Therefore, it can be assumed that there is no degradation regarding stack components like membrane, bipolar plates or porous transport layer which would increase the ohmic resistance of the stack. One can see a widening of the semi-circles with increasing number of load cycles so that it can be assumed that the degradation takes place in the catalyst layer.

3. Results

As seen in figure 1 and 2, stationary operation of both functional systems are possible. The AEL system shows no signs of degradation over the course of the experiment, while the increase of the operation temperature of the stacks in the SOEC indicates a significant degradation. The cause of this effect is not yet fully understood, but silicates in the feed water could contribute to this.

The dynamic behaviours of both plants shown in figure 3 and 4 have to be further investigated due to several, longer downtimes. Both systems tend to have a higher voltage after the dynamic profile than before. This can be explained by the decrease of the temperature, which leads to a lower efficiency of the electrolysis cells. As the temperature has a higher influence in the SOEC system, it is obvious that the voltage in the SOEC needs a longer time in comparison to the AEL to obtain its original value. A faster degradation due to dynamic operation could not be observed, but has to be investigated further.

The downtimes of the plants were mostly caused by the balance of plant of each system. Pumps, sensors and electrical components of the electrical cubicle malfunctioned and led to stop of operation for sometimes several weeks. Only in a few cases there were problems with the electrolysis stacks themselves.

Experiments could not be carried out on the PEMEL system, as it was not able to operate up to this day. After a long delay in delivery, problems with the certifications occurred on part of the manufacturer that made it impossible to conduct any testing with this system. The plant shall be tested as soon as these issues are resolved.

Regarding the PEMEL stacks figure 5 and 6 show that the degradation occurring over time are partial reversible. The results depicted in Figure 7 indicate a degradation rate of about 200 µV/h. The degradation rate one can often find in literature for the stationary operation of PEMEL stacks is in the range of 10-200 µV/h [8, 9]. While this is a preliminary result it needs further measurements in order to be approved.

Furthermore, the Nyquist plots of different temperatures shown in Figure 8 lead to the assumption that there is no degradation regarding stack components like membrane, bipolar plates or porous transport layer. It is likely that the degradation takes place in the catalyst layer. This assumption has to be investigated further with the help of ex-situ measurements.

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