# Techno-Economic Comparison of Flexibility Options in Chlorine Production

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**Abstract:** In order to allow demand side management in the chlorine industry, we suggest seven modifications to the conventional chlor-alkali process. The modifications include the oversizing of electrolyzer cells, replacement of electrodes and integration with flexible auxiliary units. We optimize the operation of the processes for four scenarios with different electricity price profiles and hydrogen prices. We then rank the processes in a merit order of three economic metrics including investment costs, operating costs and payout time. While reasonable payout times are achieved with many of the flexible processes, the best option with the shortest payout time highly depends on the prices of hydrogen and electricity. The results indicate that flexible chlor-alkali processes with-

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out auxiliary units outperform steady-state chlor-alkali processes with flexible auxiliary units. In particular, the combination of two electrodes or the implementation of a bifunctional electrode for operational mode switching seems to be the best compromise.

# 1 Introduction

Due to significant temporal fluctuations in the generation of renewable electricity, challenges for power grid stability arise [1]. One way of stabilizing the grid is by adapting the electricity demand to its provision via Demand Side Management (DSM) [2]. In DSM, energy-intensive processes are operated flexibly in order to increase their operational level when a high share of electricity from intermittent resources is available and decrease their operation when the share is low. Many publications have shown economic potential of DSM with a flexible operation of energy-intensive chemical plants, such as air separation units [3;4] and aluminium production plants [5].

Chlor-alkali (CA) electrolysis is an energy-intensive industrial process that is suited for DSM. It produces the base chemicals chlorine ($Cl_2$) and sodium hydroxide (NaOH) as well as hydrogen ($H_2$) as a byproduct in the conventional process. The fast dynamics of CA electrolysis [6] make chlorine production suitable for varying the operational level. Also, CA electrolysis in Germany consumed 4.3% of the German industrial electricity consumption in 2017 [7;8;9]. Therefore, DSM of CA electrolysis seems promising and desirable.

Energy-intensive processes can take an economic benefit from DSM by participating in either electricity spot markets or grid balancing markets, or both [5]. On the spot markets, the process can adapt its power load to the fluctuation in electricity spot prices. On the balancing markets, the process temporarily changes its power load and receive compensation payments from a transmission system operator (TSO). Particularly for CA electrolysis, Babu and Ashok [10] studied the optimal load scheduling of a conventional CA process under different time-of-use tariffs. They showed that the energy cost and peak load could be reduced by load shifting. Otashu and Baldea [11] developed a dynamic model of a membrane-based CA process and optimized its operational profiles considering the fluctuation in electricity prices. They particularly paid attention to the behavior of the cell temperature which was calculated by the heat balance models embedded. In addition to these investigations, we also examined economic viability of DSM for various CA processes where one of the following three different electrodes are implemented: a standard cathode (STC), an oxygen-depolarized cathode (ODC) demanding lower power consumption than STC, and a bifunctional electrode allowing for operational mode switching[12;13]. We found that their economic performance highly depends on electricity and hydrogen prices. Ausfelder et al.[14] roughly estimated the required compensation payments for recouping the economic losses due to the provision of the power capacity on the balancing market via diverse means for the grid balancing. They highlighted that the use of ethylene dichloride (EDC) as an energy storage material and use of the bifunctional electrode could offer the flexibility potential with the least impact on the subsequent processes. In particular, they do not necessitate increasing the conventional chlorine storage, which is very costly or even prohibited due to the strict regulations for ensuring safety[15].

However, the aforementioned strategies for DSM with the STC, ODC or bifunctional electrode face several challenges. Industrial CA processes are mostly operated at over 95% capacity utilization[14]. They can reduce the power load but cannot increase it substantially, so we cannot meet the aggregate demand in chlorine (when DSM on the spot market is of interest). Therefore, they require further investments to allow for load shifts by oversizing the process[14] which could be very costly depending on the conditions of the plant site[16]. Furthermore, for the DSM of a CA process, its downstream process also needs to adjust its operation level[17] along with an intermediate storage of the products. The novel idea of switching the operational mode of CA electrolysis using the bifunctional electrode can avoid these challenges, but substantial investment costs are incurred for retrofitting the electrolyzers as well as building additional infrastructure[12].

In order to overcome these challenges, we consider combination of the electrolyzer stacks where the STC and ODC are implemented separately, which is herein firstly introduced. Such a combination of two different electrode types with different electricity demands allow the anti-proportional change in individual production rates. This process configuration allows to change the overall electricity demand while keeping the overall chlorine production constant. Moreover, this combination does not incur additional investment costs substantially. As further options for the flexibilization, we consider the integration of a CA process with auxiliary units, such as water electrolyzer, fuel cell and battery, which provide the demanded flexibility. We can then operate the CA process at steady state without any oversizing and chlorine storage.

In this study, we will answer the question "Which option in chlorine production offers the best trade-off between low required investment costs and the highest possible economic benefit of DSM on the electricity spot market?". We consider 1) the reference of conventional process at steady state and seven options, grouped into three classes, that can flexibly operate for DSM on the electricity spot market: 2) oversized CA process with STC, 3) oversized CA process with ODC, 4) oversized CA process with the bifunctional electrode, and 5) CA process that employs both STC and ODC; and CA processes associated with 6) water electrolyzer, 7) fuel cell and 8) battery energy storage system. We assume to build a new CA process in which operational flexibility is implemented while satisfying fixed demands for the products including chlorine, sodium hydroxide, and hydrogen. In each process, only one electrochemical system is allowed to be operated dynamically so that we can clearly identify attractive systems for the provision of operational flexibility. We calculate operating margins from flexible operation (including production level change and operational mode switching) by optimizing the operation profile of each process given an electricity price time series. We then rank the processes based on a merit order of economic metrics such as investment costs, operating costs, and the payout time (POT) under various scenarios, e.g., assuming different hydrogen prices and electricity spot price profiles with an accurate forecast.

## 2 System Description

The conventional chlor-alkali electrolysis is operated with a standard cathode at steady state. In order to provide operational flexibility for DSM to this reference case, we investigate the aforementioned seven flexible CA processes as options (see Figure 1) that produce the same amount of chlorine as the reference. These options are grouped into three different classes. Class-A consists of CA electrolyzers that are oversized and that employ either the STC, ODC, their combination or the bifunctional electrode for switchability. Class-B contains the CA electrolyzers that are operated at steady state and that are combined and connected via material flow with auxiliary units including water electrolyzers (WEL) and fuel cells (FC). In Class-C the CA electrolyzers are combined with auxiliary units but not connected to these via material flow. In this last class we consider the addition of a battery electric storage system (BESS) to the CA electrolyzers for flexibility provision.

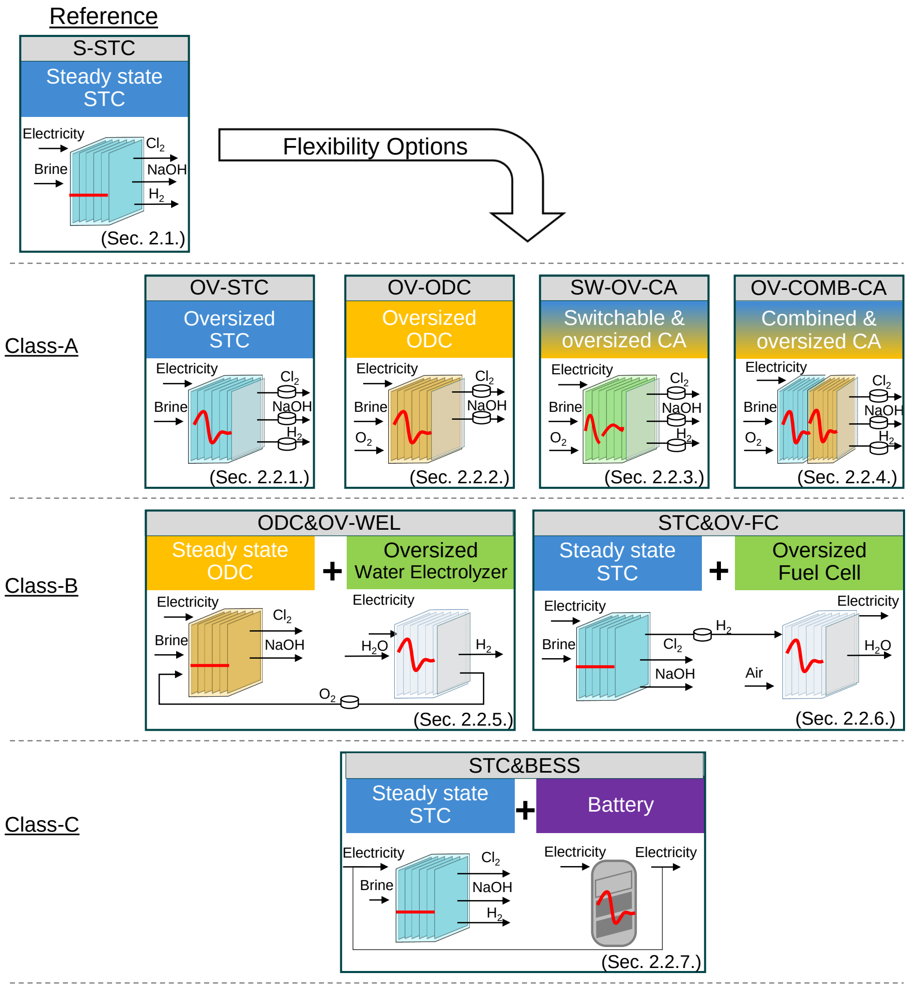


Fig. 1: Options of CA processes for providing flexibility.

**Steady State STC-based CA Process (S-STC, Reference Process):** As our reference case, we consider the conventional STC-based CA process with the nominal chlorine production rate at 100% of installed capacity, which exactly meets the downstream demand for chlorine. The net chemical reaction of the CA electrolysis with STC producing hydrogen as a byproduct is

$$2\mathrm{NaCl} + 2\mathrm{H_2O} \leftrightharpoons 2\mathrm{NaOH} + \mathrm{Cl_2} + \mathrm{H_2} \tag{1}$$

The options will produce exactly the same amount of chlorine during the considered time horizon but allow for operational flexibility with respect to electricity demand.

**Oversized STC-based CA Process (OV-STC):** The most intuitive way of providing operational flexibility to the conventional CA process is to increase the production capacity by so-called oversizing. This allows load shifts from times with high electricity prices to times with low electricity prices. Chlorine storage sets limits to the flexibility of not only OV-STC but also all the other CA processes by considering a maximum chlorine storage content.

**Oversized ODC-based CA Process (OV-ODC):** The utilization of an oxygen depolarized cathode (instead of STC) allows direct contact of the liquid electrolytic phase with a gas phase at the location of the catholytic electrochemical reaction. This strategy reduces the total cell potential and therefore the electricity demand by 30% due to a change in side reactions[18]. According to the net chemical reaction

$$2\mathrm{NaCl} + \mathrm{H_2O} + \frac{1}{2}\mathrm{O_2} \leftrightharpoons 2\mathrm{NaOH} + \mathrm{Cl_2}, \tag{2}$$

the stoichiometries of chlorine, sodium hydroxide and sodium chloride are the same as in the STC-based process. However, OV-ODC does not produce hydrogen. Furthermore, oxygen has to be provided as a reactant. Similar to OV-STC, the electrolyzers are oversized for providing the requested flexibility.

**Switchable and Oversized CA Process (SW-OV-CA):** Challenges concerning a limited chlorine tank size as well as production capacity can be overcome by utilization of the bifunctional electrode[19]. In previous studies, we already optimized the operation[12] and additionally the oversizing[13] of this novel electrolyzer which enables operational mode switching between two modes that operate according to the two above presented processes (STC and ODC). The corresponding modes are called $H_2$-mode and $O_2$-mode, respectively. The advantage of the bifunctional electrode is that the electricity demand can be changed (unlimitedly long by switching) even under limited chlorine storage capacity, in contrast to OV-STC or OV-ODC. A drawback is a certain downtime during switching for cell cleaning.

For a steady-state analysis assuming constant prices over time, Figure 2 presents breakeven prices at which the two modes of CA electrolysis result in the same operating costs. The dependence of the breakeven price on the prices of electricity and hydrogen is shown. For further information on our definition of the breakeven prices we refer to Brée et al.[12]. Note that we do not include taxes that could be imposed on electricity purchase (e.g., EEG surchage[20]). However, if taxes were to be included, the benefit of the $O_2$ mode would already start at lower electricity prices, i.e., the breakeven price line would be shifted down. The given breakeven line slightly differs from the one we presented in Brée et al.[12], as we herein updated the energy demands to newly available data and included the operating costs of water.

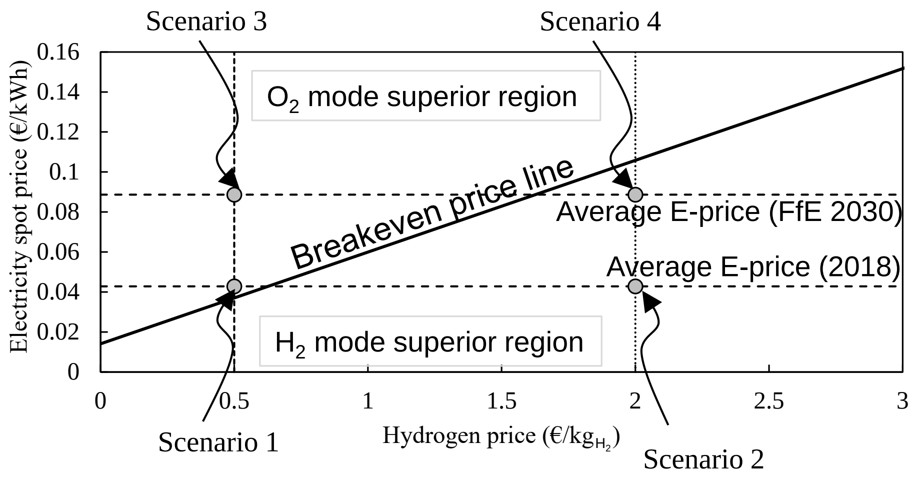


Fig. 2: Breakeven prices (solid line) at which both modes result in the same operating costs during operation at steady-state. $0.05\,€/\mathrm{kg}_{O_2}$ and $0.01\,€/\mathrm{kg}_{H_2O}$ are assumed for oxygen and water prices, respectively. The $H_2$-mode is superior to the $O_2$-mode on the right hand side of the breakeven price line. Four circles indicate the electricity and hydrogen price combinations used in the analyzed scenarios.

**Combined and Oversized CA Process (OV-COMB-CA):** A further approach is to combine STC- and ODC-based electrolyzer stacks in one plant, where a fixed share of the stacks are equipped with STCs and the remaining with ODCs. According to the breakeven price line (c.f. Figure 2), a part of the stacks will then always be in the more advantageous and the other part in the less advantageous operation. When the whole plant is oversized while keeping the shares constant, the more beneficial part of the plant can be ramped up in operation and the operation of the other part ramped down. For instance, when the electricity price is high and hydrogen price is low, chlorine is produced predominantly by the share of the ODC. However, to meet the downstream demand for chlorine, the share with the STC will still be operated - but, with lower production rate.

**ODC-based CA Process with Oversized Water Electrolyzer (ODC&OV-WEL):** Installing auxiliary units is a further approach for providing operational flexibility to the CA process. The added process is operated flexibly while the CA process is operated at steady state. The addition of a water electrolyzer to the ODC-based CA process produces hydrogen and oxygen by consuming additional electricity. The water electrolyzer is a suitable process for DSM due to its fast dynamics[21].

The water electrolyzer is based on the oxygen evolution reaction (OER):

$$H_2O \leftrightharpoons H_2 + \frac{1}{2}O_2. \tag{3}$$

The nominal capacity of the water electrolyzer is based on S-STC in order to produce exactly the same amount of hydrogen as the reference. The oxygen produced in the water electrolyzer is used as a reactant in the CA process. A storage tank for oxygen between both processes allows varying the operation level of the water electrolyzer if this is oversized.

In this study we assume the installation of an alkaline water electrolyzer as this is, according to the International Energy Agency[22], the most mature technology for water electrolysis. The limiting storage material for flexibilization in this process would be oxygen.

**STC-based CA Process with Oversized Fuel Cell (STC&OV-FC):** A similar approach as ODC&OV-WEL can be realized with the combination of STC-based CA process at steady state and a dynamically operating fuel cell. A fuel cell can provide electricity to the CA process or sell it to the spot market via the reversed OER (Equation (3)). We assume the same prices for selling as for buying electricity and therefore calculate the net electricity consumption. Campanari et al. already described the benefit of energy and emission savings when coupling a CA process via hydrogen, electricity and heat integration with a fuel cell[23].

The nominal capacity of the fuel cell is based on the reference case in order to consume exactly the amount of produced hydrogen. STC&OV-FC therefore does not depend on the hydrogen price. Storage of hydrogen between the two processing units allows variation of the operation level of the fuel cell if it is oversized. We assume the installation of a proton exchange membrane (PEM) fuel cell because of its high power capacity and current density, long lifetime, and fast response time[22]. Air is supplied to the fuel cell as the source of oxygen. The limiting storage material for flexibilization of this process would be hydrogen.

**STC-based CA Process with Battery (STC&BESS):** Another rather intuitive approach for providing electrical flexibility to the CA process is the introduction of a battery electric storage system. This approach aims to benefit from the strong capability of BESS to shift electric loads over time and the resulting potential to save overall electricity costs. This process concept was introduced as a so-called virtual power plant for chlorine production in Ausfelder et al.[14].A redox flow battery is a promising technology for large-scale chemical electricity storage as the storage capacity is individually scalable from the reactive system components[24]. Of the several existing redox flow battery chemistries, the vanadium redox flow battery (VRB) is the most mature with systems operated at megawatt scale[25].

## 3 Modelling the Process Options

We develop and use lumped and quasi-steady-state models with discrete time for determining the optimal operation of the CA processes. The models for all the process options commonly comprise four elements: (1) Mass balances of the electrochemical processes and intermediate storage; (2) power functions that calculate electric energy consumption or production; (3) operational constraints that characterize ramping and mode transitions; and (4) cost functions that calculate the three economic metrics including operating costs, investment costs, and payout times. The operating costs include purchasing costs or benefits of electricity, hydrogen, oxygen and water. For determining the optimal operation, we minimize the operating costs over a given time horizon. These models are taken from Brée et al.[12], Roh et al.[13], Nguyen et al.[26] and Kuhlmann[27] and were slightly modified. The models and the required changes are documented in Section 1 of the Supporting Information (SI).

# 4 Comparison of the Process Options

After an introduction of the analyzed scenario, we firstly compare the operating costs of the flexible CA processes running at steady-state. We then determine the optimal operation profiles considering fluctuating electricity spot prices, compare the three economic metrics (operating costs, investment costs and payout times) of the processes and rank them accordingly.

## 4.1 Scenario Description

**Power Capacity and Oversizing Factor** The CA processes produce the same amount of chlorine but differ in power capacity. The power capacity of the reference case (S-STC) is set to 50 MW, which is the average capacity of industrial CA processes employing membrane cells in Europe[8]. This results in chlorine production of 21.9 t/h for all the processes. Other mass flows such as hydrogen and oxygen are given in Table S1 of the SI.

Table 1: Power capacity and oversizing factor of the seven flexibility options.

| Overcapacity | Specification | Flexibility option: OV-STC | OV-ODC | SW-OV-CA | OV-COMB-CA | STC&OV-FC | ODC&OV-WEL | STC&BESS |
|---|---|---|---|---|---|---|---|---|
| | Nominal capacity for total process (capacity for auxiliary unit), MW | 50.00 | 36.42 | 50.00 | 43.21 | 48.11 (9.46) | 68.86 (32.43) | 50.00 |
| **2.5MW** | Total capacity, MW | 52.50 | 38.92 | 52.50 | 45.71 | 46.94 | 71.36 | 52.50 |
| **5MW** | | 55.00 | 41.42 | 55.00 | 48.21 | 46.31 | 73.86 | 55.00 |
| **10MW** | | 60.00 | 46.42 | 60.00 | 53.21 | 45.03 | 78.86 | 60.00 |
| **2.5MW** | Oversizing factor for auxiliary unit, % | N/A | | | | 26.42 | 7.71 | N/A |
| **5MW** | | | | | | 52.85 | 15.42 | |
| **10MW** | | | | | | 105.70 | 30.83 | |
| **2.5MW** | Oversizing factor for total process, % | 5.00 | 6.86 | 5.00 | 5.79 | N/A | 3.63 | |
| **5MW** | | 10.00 | 13.73 | 10.00 | 11.57 | | 7.26 | |
| **10MW** | | 20.00 | 27.45 | 20.00 | 23.14 | | 14.52 | |

We consider three different overcapacities: 2.5, 5 and 10 MW that correspond to 5, 10 and 20 % of the nominal capacity of S-STC. The ODC-based CA process demands lower electricity than the STC-based one when the same amount of chlorine should be produced, so the former requires a lower nominal capacity. In order to provide the same level of overcapacity in MW, we apply a higher oversizing factor to the process with ODC than the process with STC. We assume that the combined CA process employs STC and ODC by 1:1. Therefore, the oversizing factor has a value between those of the CA processes solely with STC and ODC. For the switchable CA process, an optimization determines the current operational mode which could be $H_2$-mode for the entire time horizon. Therefore, the capacity is chosen according to this mode, i.e. to be 50 MW, with oversizing of, e.g., 10 % for 5 MW overcapacity. The nominal capacities of the fuel cell and water electrolyzer are based on the hydrogen production of S-STC and respective power function and size of the process given in literature (see Section 1.1 of the SI). Note that they should consume or produce exactly the amount of hydrogen obtained from S-STC. The nominal capacity of the fuel cell is much smaller (9.46 MW) than other processes, so the oversizing factor for the fuel cell is relatively high (e.g., 52.85 % for 5 MW overcapacity). Note that the total capacity of STC&OV-FC is lower than 50 MW because of the supplementary power generation by the fuel cell. The battery has rated power of 2.5, 5 and 10 MW and can store electricity for a maximum of three hours that result in the shortest payout time. Detailed information about the capacities and oversizing factors are given in Table S1 of the SI.

**Operational Parameters** We assume that the size of the storage tank for chlorine is limited but those for hydrogen and oxygen are unlimited. All the operational parameters such as ramping and cell cleaning duration for CA electrolyzers, maximum duration for chlorine storage, and allowable current densities are given in Table S2 of the SI.

**Electricity and Material Prices** We introduce two different profiles of electricity spot prices (see Figure 5). One profile is from the German EPEX

SPOT market, recorded end of May in 2018[28]. Its average price is 0.043 €/kWh. The second electricity price profile is a week taken from a prediction for the year 2030 estimated by Kern et al.[29]. Its fluctuations are high within the range of [0;1.5] €/kWh. Note that we exclude taxes imposed on electricity purchase such as EEG surcharge[20] or any potential benefits from additional energy market regulations such as the german so-called "7,000-hour-rule" (in German: "7000-Stunden-Regel")[30].

Hydrogen prices of 0.5 €/$kg_{H_2}$ for coal gasification and 2 €/$kg_{H_2}$ for natural gas (NG) reforming are considered. Oxygen and water prices are fixed at 0.05 €/$kg_{O_2}$ and 0.01 €/$kg_{H_2O}$, respectively, because they are not as influential on the optimal solution[12]. The four possible combinations of the two different electricity price profiles and the two hydrogen prices are named Scenario 1-4 according to Table 2 and will be considered in the process comparison. We assume that the specific prices for purchase and sale are the same.

Table 2: Description of four scenarios in the case study

| | **Electricity spot price profile** | **Hydrogen price (€/$kg_{H_2}$)** |
|---|---|---|
| **Scenario 1** | 2018 record | 0.5 |
| **Scenario 2** | 2018 record | 2.0 |
| **Scenario 3** | 2030 forecast | 0.5 |
| **Scenario 4** | 2030 forecast | 2.0 |

**Investment Costs** We estimate the investment costs of the processes based on literature data, taken from Arnold et al.[16] for expanding the capacity of an existing CA process, for the switchability from Covestro Deutschlang AG[31], for an alkaline water electrolyzer as well as for a PEM fuel cell from the International Energy Agency[22] and for the VRB from Schmidt et al.[32]. Details and a summarizing table (Table S3) are given in Section 2.3 of the SI.

## 4.2 Analysis of Operation at Steady State

We first compare the operating costs of the seven flexible CA processes running at steady-state. In other words, the processes do not employ oversizing but operate at their nominal levels with full utilization rates.

As shown in Figure 3 and as expected, the operating costs are highly dependent on the prices of electricity and hydrogen. STC-based processes are beneficial when the price of electricity is low and that of hydrogen is high. In contrast, ODC-based processes are economically preferable at high electricity prices and low hydrogen prices. These trends can also be seen in the plot of the breakeven price line (Figure 2). The operating costs in OV-COMB-CA are located in the middle of the operating costs of OV-STC and OV-ODC because of the combination ratio of 1:1.

The mass balances of both OV-STC and ODC&OV-WEL are exactly the same, but the nominal power of the former is lower by 27 %. This is due to a high overpotential of the oxygen evolution reaction[33] in OV-ODC and WEL. It results in low cell efficiencies of ODC-CA (61.8 %[31]) and WEL (72.4 %[34]) at their maximal current densities compared to STC-CA (80.1 %[31]) and thus always higher operating costs. All the cell efficiencies are calculated from data available in the respective literature. Similarly, the mass balances of both OV-ODC and STC&OV-FC are exactly the same, but the former represents a lower nominal power by 10 %. This is mainly due to the low system efficiency of the PEM fuel cell (50 %[35]) despite the high cell efficiency of STC-CA. However, the considered fuel cell does not require oxygen purchase but is operated with air which is free of charge. Thus, the operating costs of STC&OV-FC are lower than those of OV-ODC when electricity is cheap. However, as the produced hydrogen of the CA electrolysis is consumed internally and is no longer available for sale, STC&OV-FC is less favourable when hydrogen prices are high.

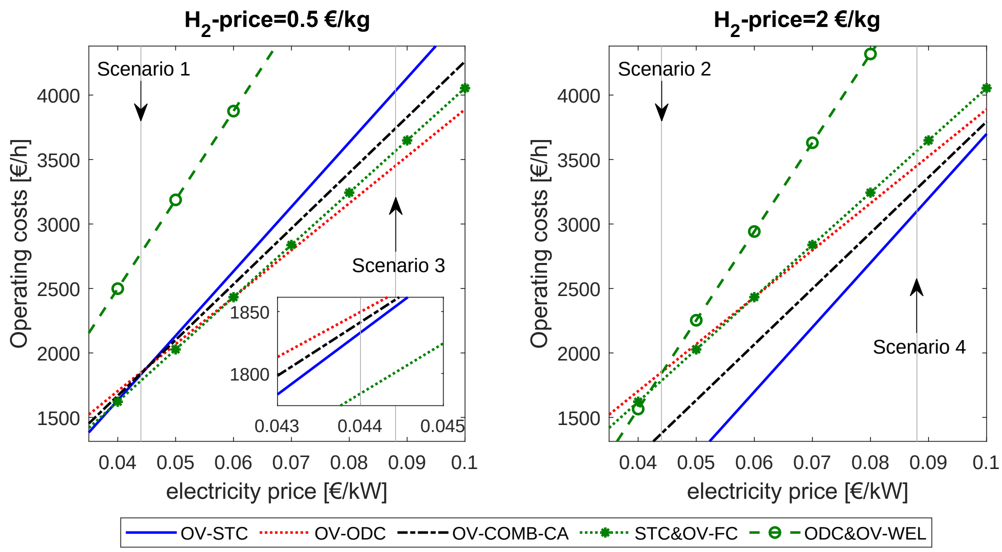


Fig. 3: Operating costs of the flexible CA processes at steady state with respect to electricity prices for two different prices of hydrogen. At steady state, the operating costs of OV-STC are equal to S-STC and to STC&BESS (the battery is inactive). SW-OV-CA does not switch its operational mode at steady state and its operating costs are therefore equal to the operating costs in the more beneficial mode. The exact values of the operating costs for all the processes in each scenario are given in Table S4 of the SI.

## 4.3 Analysis of Flexible Operation

We solve optimization problems to determine the optimal operational profiles of the flexible processes considering fluctuations in electricity spot prices. Also, the economic metrics of the processes are compared to identify promising DSM strategies in each scenario.

### 4.3.1 Modeling and Optimization Strategy

We consider one week as the time horizon for all the processes. Time steps of one hour are assumed for the auxiliary units. This discretization is in accordance with the hourly updated electricity prices at the spot market and therefore sufficient for the optimization. For the CA process, however, we choose 10 minutes intervals because of the cell cleaning (taking less than an hour) and the ramping constraints.

As is commonly done, e.g. in Brée et al.[12], we approximate the nonlinear power functions of the electrochemical processes using piecewise linear functions. Thus we obtain mixed-integer linear programs (MILPs) which can be solved with commercial solvers. For the PEM fuel cell we directly use the nonlinear model as the corresponding mixed-integer nonlinear program (MINLP) is readily solved. For the redox flow battery, we linearize the charging and discharging functions with respect to the rated power.

In order to determine optimal operation profiles, we formulate optimization problems in GAMS 28.2.0 and solve them using BARON[36] for the fuel cell case (MINLP) and IBM ILOG CPLEX 12.9.0.0 for the others (MILP).

#### 4.3.2 Optimal Operation Profiles

Figure 4 presents the optimal power demand profiles for all processes determined by solving the optimization problems of Scenario 1. The optimal profiles of Scenario 4 (Figure S2) can be found in the SI. Note that the profiles of Scenario 2 and 3 are omitted because the optimal profile of most processes (except for SW-OV-CA and OV-COMB-CA) are the same as in Scenario 1 and 4, respectively, as they only depend on the electricity price and not on the different hydrogen prices. SW-OV-CA, however, does not switch its operational mode in Scenario 2 and 3 but operates the same as OV-STC in Scenario 1 and OV-ODC in Scenario 4, respectively (see Figure 2). The results of OV-COMB in all the scenarios are shown in Figure 5. In order to minimize the weekly operating costs, the power demand of the oversized (and switchable) processes varies over time considering the fluctuation in electricity prices. The variations are higher for the price profile of 2030 as it fluctuates more sharply.

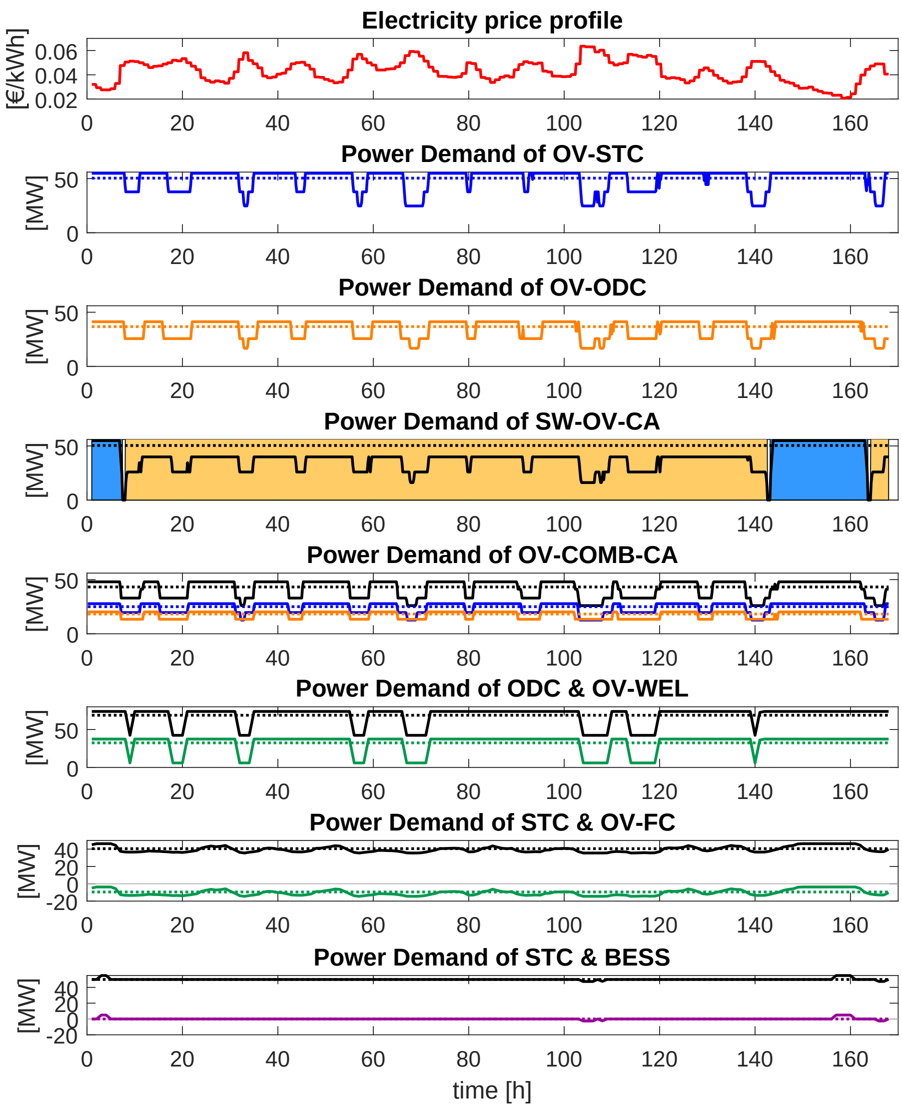


Fig. 4: Optimal power demand profiles for 5 MW overcapacity in Scenario 1. The negative value indicates power generation (e.g., fuel cell and battery). Dashed line: Nominal power demand or consumption. — Black line : Total power demand. — Blue line: STC CA electrolyzer. — Orange line: ODC CA electrolyzer. — Green line: water electrolyzer and fuel cell. — Purple line: Solely battery. Blue area: operation of bifunctional electrode in $H_2$-mode. Orange area: operation of bifunctional electrode in $O_2$-mode.

For the combined CA process, the CA electrolyzers with STC and ODC behave similar to OV-STC and OV-ODC, i.e., the power demand increases when the electricity price is low and vice versa. However, the strength of the fluctuation in power demand of each electrolyzer additionally depends on the price of hydrogen. For example, if the $H_2$-mode is economically more favorable than the $O_2$-mode (e.g., Scenario 2), the current density of the STC-based CA process stays at the maximum allowable level as long as possible while the current density of the ODC one fluctuates wildly (Figure 5). The opposite behavior can be found in Scenario 3 where the $O_2$-mode is superior. In Scenario 1 and 4, the prices of electricity and hydrogen are very close to the breakeven price line and thus both electrolyzers produce almost the same amount of chlorine.

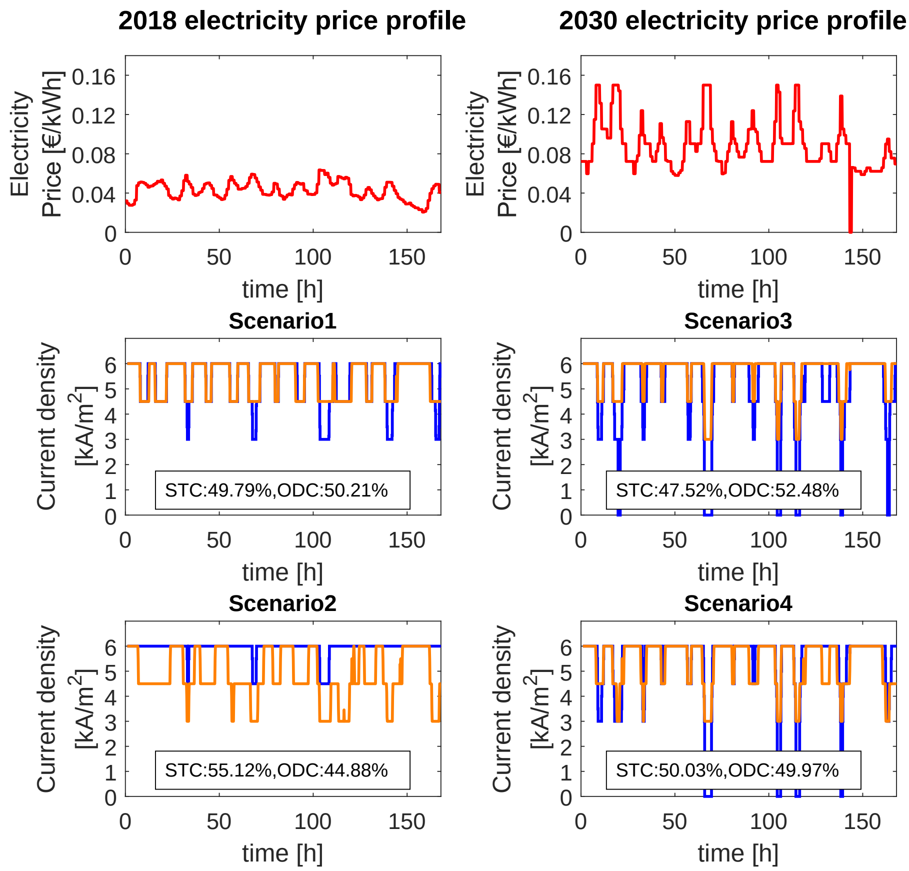


Fig. 5: Optimal current density profiles of the combined and oversized CA process for 5 MW overcapacity. The numbers in the text-box indicate how much share of chlorine is produced by each type of the CA electrolyzers.

For the switchable CA process, the operational mode switching is observed when the electricity price crosses the breakeven price line. The battery is found to be rarely active in all scenarios. The reason is that the fluctuation in electricity prices is not strong enough to compensate for the energy loss during charging and discharging by the monetary benefit expected. Improving the round-trip efficiency of the battery through further research will lead to more active operation in the future.

The flexible operation leads to savings in the operating costs for all the processes with respect to the non-oversized processes themselves (see Figure S3 in the SI). A larger overcapacity and stronger fluctuation in electricity prices bring higher savings in operating costs. Note that operating costs of both the switchable and combined CA process are dependent on the prices of electricity and hydrogen.

### 4.3.3 Process Comparison via Three Economic Metrics

In order to compare the economic metrics of the seven options for flexible operation of CA electrolysis, this section is dedicated to the evaluation of the necessary investment costs, the operating costs and the resulting payout time w.r.t. the reference case.

**Investment Costs** The investment costs for each process and each amount of overcapacity are given in Figure 6. The investment costs increase with increasing overcapacity in all cases. Firstly looking at the sole CA processes without auxiliary units, OV-STC incurs the lowest additional investment costs, followed by OV-COMB-CA. With the 1:1 ratio in the electrolyzer types, OV-COMB-CA requires the average investment costs of OV-STC and OV-ODC. SW-OV-CA requires higher investment costs than all the other sole CA processes due to the retrofit with bifunctional electrodes. Regarding the addition of auxiliary units, STC&BESS requires the lowest investment costs and is on second rank compared to all flexible processes. The highest investment costs, i.e., about twice as high compared to the reference case (S-STC), are incurred by the additional units WEL and FC, whereas building STC&OV-FC is more expensive than ODC&OV-WEL for all overcapacities. Even though the nominal and oversized capacities of the FC are much lower than of the WEL, the high specific capital investment of the type of the considered fuel cell (PEMFC) results in the highest investment costs.

Figure 6 also presents the uncertainty within the investment costs. Details on the calculation of the uncertainties is given in Section 2.3 of the SI.

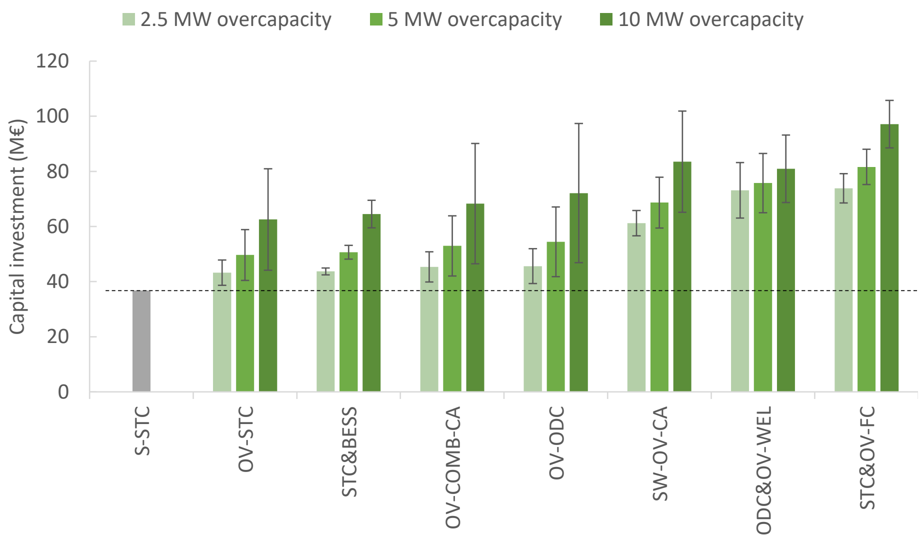


Fig. 6: Merit-order of the investment costs for the different overcapacity for flexible operation. The ranking is based on the values for 5 MW overcapacity. The bars indicate the uncertainty.

**Operating Costs** The weekly operating costs considering earnings and expenditures for electricity, hydrogen, oxygen and water are presented in Figure 7. The overcapacity has a minor influence on the results while the influence of the electricity price profile and hydrogen price predominate. According to Section 4.3.2, oversizing always results in operating cost savings with respect to the same non-oversized process itself, which is why OV-STC always results in lower operating costs than S-STC. SW-OV-CA is able to operate in the mode that is more beneficial and even switch between the modes and therefore results in lower operating costs than the reference case in all scenarios. STC&BESS always results in only slightly lower operating costs than the reference which is due to the fact that the VRB is barely operated resulting in almost exclusive steady state operation of STC as presented in Section 4.3.2. The operating costs of the remaining processes (OV-ODC, OV-COMB-CA, STC&OV-FC) are higher or lower than the reference depending on the combination of electricity price profile and hydrogen price.

The resulting merit order of the flexible processes is in accordance with the merit order of the processes operated at steady state (cf. Section 4.2). The merit-order in Scenario 1 starts with STC&OV-FC. The operating costs of ODC&OV-WEL are much higher than those of all the other processes in Scenario 1, 3 and 4. In Scenario 2, the $H_2$-mode is by far superior to the $O_2$-mode so that OV-STC is economically favorable over OV-ODC. In contrast, the latter process is the best option in Scenario 3. In Scenario 4, the best options, SW-OV-CA and OV-STC, are equally beneficial. OV-COMB-CA is always less beneficial than the sole preferable mode, but is more beneficial than the unfavorable mode.

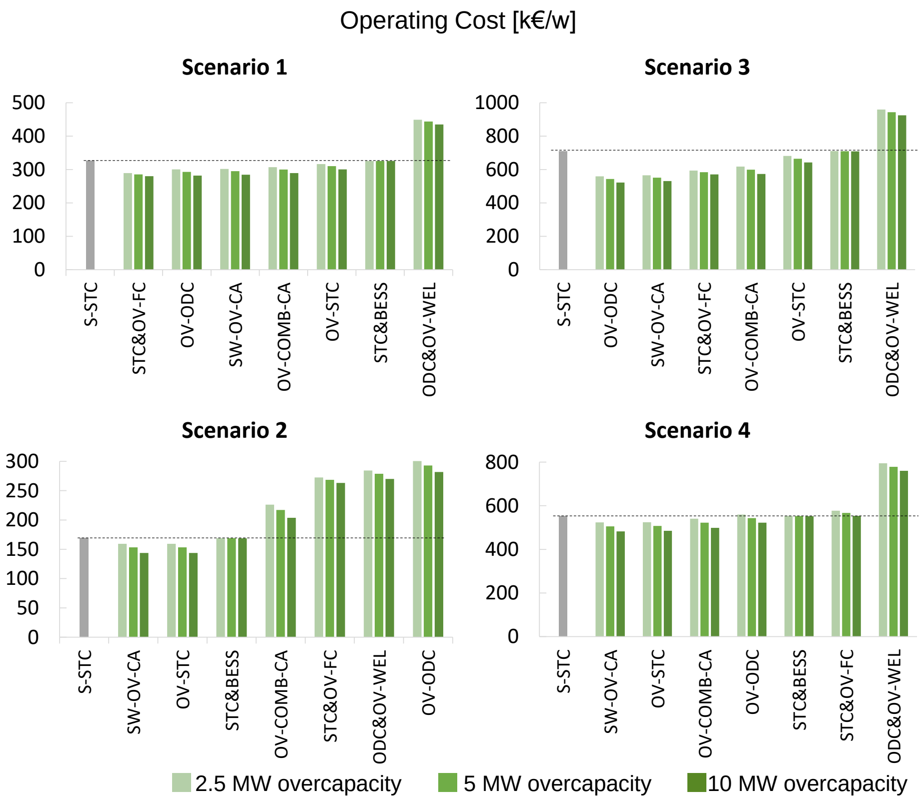


Fig. 7: Merit-order of the operating costs considering earnings or expenditures for electricity, hydrogen, oxygen and water with various electricity price profiles, hydrogen prices and different overcapacities.

**Payout Times** The payout time combines the considerations of additional investment costs and operating cost savings. Figure 8 presents the payout times for all the flexible processes for the above introduced scenarios and flexibilities. For the processes that resulted in higher operating costs compared to the reference case, payout times are not calculated as they are not economically favourable at all.

For all the processes, the reachable payout times are shorter in 2030 (Scenario 3 and 4) than in 2018 (Scenario 1 and 2) due to the higher operating cost savings. The payout times for STC&BESS exceed 250 years for all scenarios. Thus, STC&BESS is not economically interesting unless the investment costs will be decreased significantly and/or the round-trip efficiencies will be improved. Note that the payout time of STC&BESS with three different overcapacities is the same because the investment cost for the battery and the operating cost saving are linearly proportional to the overcapacity.

The merit order of the remaining processes is different in all scenarios. In the scenarios with a low hydrogen price (Scenario 1 and 3), the four processes with the shortest payout time in ascending order are: OV-ODC (2.5 MW), OV-COMB-CA (2.5 MW), OV-ODC (5 MW), OV-COMB-CA (5 MW) with payout times in the range of ∼7 to ∼12 years in Scenario 1 and ∼1 to ∼3 years in Scenario 3. Even though these processes did not have the highest operating cost savings in these scenarios, the ratio of investment costs to operating cost savings is the lowest. Compared to typical lifetimes of 15 to 20 years of the CA electrolyzer cells, these results indicate that these approaches for providing flexibility are economically beneficial in that scenario.

In Scenario 3, the high operating cost savings of SW-OV-CA make this process economically viable to reach rank 5 with ∼3 years payout time, despite its high investment costs. Only on rank 8, the first time OV-STC appears with 2.5 MW overcapacity. All payout times of this scenario (except for STC&BESS) are below 9 years.

In Scenario 2 only the following processes lead to positive savings in the operating costs with the merit order (shown in Figure 7) : SW-OV-CA, OV-STC and STC&BESS and increasing flexibilities, respectively. Due to the much higher investment costs of SW-OV-CA, this process is succeeded by OV-STC in terms of payout time.

Even though SW-OV-CA leads to the highest operating cost savings in Scenario 4, the high investment costs make this option inferior to OV-STC and OV-COMB-CA regarding payout time. The remaining processes lead to payout times >20 years or are economically not favourable at all.

Considering the uncertainty in future electricity and hydrogen prices, oversizing OV-COMB-CA seems to be the promising option for the herein chosen scenarios as this process is among the top candidates in almost all scenarios. However, if future electricity prices will be characterized by even higher fluctuations around the breakeven price line, the switchable process might turn out as the better compromise.

Payout times and the economic benefit highly depend on the chosen overcapacity. For instance, oversizing OV-COMB-CA by 5 MW in Scenario 4 leads to shorter pay-out time than oversizing this process by 2.5 or 10 MW. This means that a minimum in payout time w.r.t. the extent of oversizing must be close to oversizing by 5 MW. Therefore, optimization of the extent of oversizing is not trivial, but recommended. The authors refer to a publication, where they already showed optimal oversizing for OV-STC and SW-OV-CA [13].

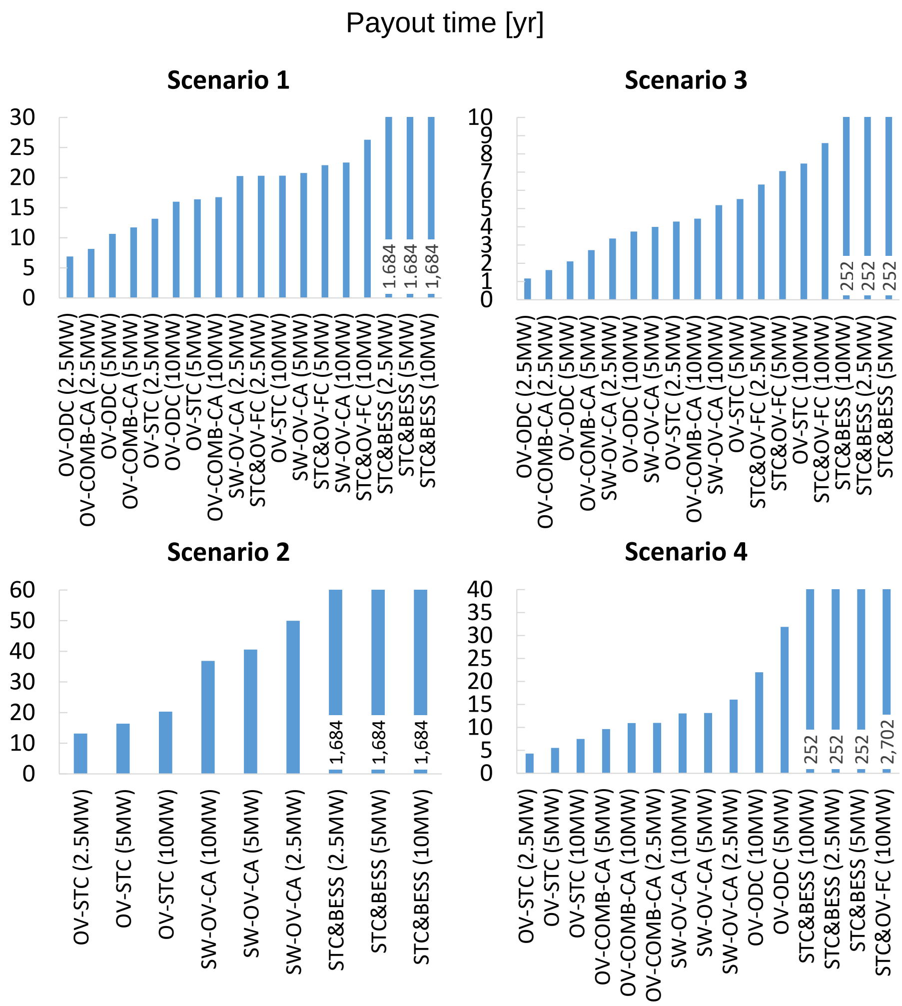


Fig. 8: Merit-order of the payout times considering the above presented investment costs and operating cost savings w.r.t the reference case (S-STC) for various electricity price profiles and hydrogen prices. We omit the bars for those processes that cannot save operating costs with respect to the reference case. The payout times are determined based on the nominal investment costs given in Table S3 of the SI.

# 5 Conclusion

We propose seven options of chlor-alkali processes that can operate flexibly for demand side management. The flexible processes adopt overcapacity and (optionally) switchability to the chlor-alkali electrolyzer or are integrated with auxiliary units that operate flexibly. In order to analyze the economic performance of their flexible operation, we optimize the operational profile of the processes while the weekly operating costs are minimized.

Each process option incurs different investment costs for employing the same level of overcapacity. The operating cost savings from flexible operation with respect to the reference case highly depend on the prices of electricity and hydrogen. Oversizing the chlor-alkali process with the standard cathode leads to relatively short payout times in all the scenarios while oversizing the process with the oxygen-depolarized cathode gets beneficial only if electricity is expensive and hydrogen is cheap. Adopting the switchability to the chlor-alkali process can reduce the operating costs in all the scenarios. However, its high investment costs for the plant retrofit that result in long payout times is a big hurdle. Combining the two electrodes in one process is a reasonable approach because it is ranked with high priority in most of the scenarios in terms of payout time. Large capital investment and low energy efficiency for water electrolyzer, fuel cell, and redox flow battery are major barriers for economical demand side management because they cannot be compensated for by the operating cost savings or require unrealistically long payout times. These processes should be improved by further R&D to reduce the capital investment and enhance the energetic efficiency. Finally, optimizing the overcapacity that maximizes the economic benefit of the flexible operation is found to be highly recommended.

As future work, other options for demand side management in chlorine production could be examined. Possible options are, e.g., air separation units that flexibly produce and supply the oxygen feedstock[4;37] to the chlor-alkali process with the oxygen-depolarized cathode (including the combined and switchable processes) or electric furnaces that flexibly produce steam that is used for the sodium hydroxide concentration unit.

Moreover, the economic viability of the (promising) flexible chlor-alkali processes could be analyzed over their lifetimes instead of one exemplary week. Böing and Regett[38] anticipated that the marginal power generation costs in Germany will rise and their fluctuation will get stronger by 2050. In addition, the demand for hydrogen as energy carrier, fuel, or chemical feedstock will grow in the future[39], so the future price of hydrogen would deviate from the present price and probably even sharply fluctuate. Particularly for the combined chlor-alkali process, the share of each type of the electrolyzers can be optimized.

Lastly, we can optimize the oversizing of all possible flexibility options for chlor-alkali electrolysis simultaneously by applying superstructure-based optimization. This will lead to the most economical performance by considering the trade-off between the flexibility options.

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## References

[1] Regelleistung, REGELLEISTUNG.NET - Internetplattform zur Vergabe von Regelleistung. https://www.regelleistung.net/, 2019; Data accessed: 18-Feb-2020.

[2] Mitsos, A.; Asprion, N.; Floudas, C. A.; Bortz, M.; Baldea, M.; Bonvin, D.;

Caspari, A.; Schäfer, P. Challenges in process optimization for new feedstocks and energy sources. *Computers & Chemical Engineering* **2018**, *113*, 209–221.

[3] Zhang, Q.; Grossmann, I. E.; Heuberger, C. F.; Sundaramoorthy, A.; Pinto, J. M. Air separation with cryogenic energy storage: Optimal scheduling considering electric energy and reserve markets. *AIChE Journal* **2015**, *61*, 1547–1558.

[4] Pattison, R. C.; Touretzky, C. R.; Johansson, T.; Harjunkoski, I.; Baldea, M. Optimal process operations in fast-changing electricity markets: Framework for scheduling with low-order dynamic models and an air separation application. *Industrial & Engineering Chemistry Research* **2016**, *55*, 4562–4584.

[5] Schäfer, P.; Westerholt, H. G.; Schweidtmann, A. M.; Ilieva, S.; Mitsos, A. Model-based bidding strategies on the primary balancing market for energy-intense processes. *Computers & Chemical Engineering* **2019**, *120*, 4–14.

[6] O'Brien, T. F.; Bommaraju, T. V.; Hine, F. *Handbook of chlor-alkali technology*; Developments in Hydrobiology; Springer: Dordrecht, 2007.

[7] Klaucke, F.; Karsten, T.; Holtrup, F.; Esche, E.; Morosuk, T.; Tsatsaronis, G.; Repke, J.-u. Demand Response Potenziale in der chemischen Industrie. *Chemie Ingenieur Technik* **2017**, *89*, 1133–1141.

[8] Euro Chlor, Chlor-alkali Industry Review 2017/2018 - Manufacturing & Applications. https://chlorineindustryreview.com/manufacturing-applications/, 2019; Data accessed: 18-Feb-2020.

[9] Appunn, K.; Bieler, F.; Wettengel, J. Germany's energy consumption and power mix in charts. https://www.cleanenergywire.org/factsheets/germanys-energy-consumption-and-power-mix-charts, 2018; Data accessed: 01-Jul-2019.

[10] Babu, C. A.; Ashok, S. Peak load management in electrolytic process industries. *IEEE Transactions on Power Systems* **2008**, *23*, 399–405.

[11] Otashu, J. I.; Baldea, M. Demand response-oriented dynamic modeling and operational optimization of membrane-based chlor-alkali plants. *Computers & Chemical Engineering* **2019**, *121*, 396–408.

[12] Brée, L. C.; Perrey, K.; Bulan, A.; Mitsos, A. Demand side management and operational mode switching in chlorine production. *AIChE Journal* **2019**, *65*, e16352.

[13] Roh, K.; Brée, L. C.; Perrey, K.; Bulan, A.; Mitsos, A. Flexible operation of switchable chlor-alkali electrolysis for demand side management. *Applied Energy* **2019**, *255*, 113880.

[14] Ausfelder, F.; Seitz, A.; von Roon, S. *Flexibilitätsoptionen in der Grundstoffindustrie*; DECHEMA, Gesellschaft für Chemische Technik und Biotechnologie eV, 2018.

[15] Holtrup, F. *Potenzial für Demand Side Management der energieintensiven Industrie in Deutschland - Eine Kostenbetrachtung am Beispiel der Chlor-Alkali-Elektrolysen*; 2015.

[16] Arnold, K.; Janßen, T.; Echternacht, L.; Höller, S.; Voss, T.; Perrey, K. FlexInd: Flexibilisation of industries enables sustainable energy systems - Final report, Wuppertal, Germany. 2016; https://wupperinst.org/fa/redaktion/downloads/projects/FlexInd_report.pdf.

[17] Hoffmann, C.; Weigert, J.; Esche, E.; Repke, J.-U. Towards demand-side management of the chlor-alkali electrolysis: Dynamic, pressure-driven modeling and model validation of the 1,2-dichloroethane synthesis. *Chemical Engineering Science* **2020**, *214*, 115358.

[18] Jung, J.; Postels, S.; Bardow, A. Cleaner chlorine production using oxygen

depolarized cathodes? A life cycle assessment. *Journal of Cleaner Production* **2014**, *80*, 46–56.

[19] Bulan, A.; Weber, R.; Bienen, F. Bifunctional electrode and electrolysis device for chlor-alkali electrolysis. Patent WO 2017/174563 A1. 04.04.2017.

[20] BMWi, State-imposed components of the electricity price. https://www.bmwi.de/Redaktion/EN/Artikel/Energy/electircity-price-components-state-imposed.html, 2020; Data accessed: 03-Mar-2020.

[21] Buttler, A.; Spliethoff, H. Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review. *Renewable and Sustainable Energy Reviews* **2018**, *82*, 2440–2454.

[22] International Energy Agency, Technology roadmap hydrogen and fuel cells. https://www.iea.org/publications/freepublications/publication/TechnologyRoadmapHydrogenandFuelCells.pdf, 2015.

[23] Campanari, S.; Guandalini, G.; Coolegem, J.; ten Have, J.; Hayes, P.; Pichel, A. H. Modeling, Development, and Testing of a 2 MW Polymeric Electrolyte Membrane Fuel Cell Plant Fueled With Hydrogen From a Chlor-Alkali Industry. *Journal of Electrochemical Energy Conversion and Storage* **2019**, *16*, 73.

[24] Chakrabarti, M. H.; Mjalli, F. S.; AlNashef, I. M.; Hashim, M. A.; Hussain, M. A.; Bahadori, L.; Low, C. T. J. Prospects of applying ionic liquids and deep eutectic solvents for renewable energy storage by means of redox flow batteries. *Renewable and Sustainable Energy Reviews* **2014**, *30*, 254–270.

[25] Pan, F.; Wang, Q. Redox species of redox flow batteries: A review. *Molecules* **2015**, *20*, 20499–20517.

[26] Nguyen, T. A.; Byrne, R. H.; Chalamala, B. R.; Gyuk, I. Maximizing the revenue of energy storage systems in market areas considering nonlinear storage efficiencies. 2018 International Symposium on Power Electronics, Electrical Drives, Automation and Motion (SPEEDAM). 2018; pp 55–62.

[27] Kuhlmann, J. Optimal integration of a battery with the chlor-alkali process for demand side management. Bachelor thesis, RWTH Aachen University, 2019.

[28] Agora Energiewende, https://www.agora-energiewende.de/de/themen/-agothem-/Produkt/produkt/76/Agorameter/, 2019; Data accessed: 15-Nov-2019.

[29] Kern, T.; Böing, F.; von Roon, S. Merit Order Netz-Ausbau 2030 - Preiszeitreihe Basisszenario. München: Forschungsgesellschaft für Energiewirtschaft mbH. https://www.ffe.de/themen-und-methoden/speicher-und-netze/521-merit-order-netz-ausbau-2030-mona-2030, 2018.

[30] Smart Power GmbH, Die 7000-Stunden-Regel. https://www.smart-power.net/de/einsatzgebiete/7000-stunden, 2020; Data accessed: 03-Mar-2020.

[31] Personal Communication with Covestro Deutschland AG, 2018.

[32] Schmidt, O.; Melchior, S.; Hawkes, A.; Staffell, I. Projecting the future levelized cost of electricity storage technologies. *Joule* **2019**, *3*, 81–100.

[33] Moussallem, I.; Jörissen, J.; Kunz, U.; Pinnow, S.; Turek, T. Chlor-alkali electrolysis with oxygen depolarized cathodes: history, present status and future prospects. *Journal of Applied Electrochemistry* **2008**, *38*, 1177–1194.

[34] Roy, A.; Watson, S.; Infield, D. Comparison of electrical energy efficiency of atmospheric and high-pressure electrolysers. *International Journal of Hydrogen Energy* **2006**, *31*, 1964–1979.

[35] Hydrogenics, HyPM fuel cell power modules. https://www.h2fc-fair.com/hm10/images/pdf/hydrogenics02.pdf, 2010; Data accessed: 18-Feb-2020.

[36] Khajavirad, A.; Sahinidis, N. V. A hybrid LP/NLP paradigm for global optimization relaxations. *Mathematical Programming Computation* **2018**, *10*, 383–421.

[37] Caspari, A.; Offermanns, C.; Schäfer, P.; Mhamdi, A.; Mitsos, A. A flexible air separation process: 2. Optimal operation using economic model predictive control. *AIChE Journal* **2019**, *65*.

[38] Böing, F.; Regett, A. Hourly CO2 emission factors and marginal costs of energy carriers in future multi-energy systems. *Energies* **2019**, *12*, 2260.

[39] IEA Hydrogen, Global trends and outlook for hydrogen. https://ieahydrogen.org/pdfs/Global-Outlook-and-Trends-for-Hydrogen_Dec2017_WEB.aspx, 2017.

## Abstract Graphics - For Table of Contents Only