

# Demand Side Management and Operational Mode Switching in Chlorine Production

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*Demand side management (DSM) gains importance due to penetration of renewable energy in energy provision. A promising candidate is the chlor-alkali process as it is an energy-intensive process with a high installed capacity and high penetration worldwide. In this article, we consider DSM for the purpose of chlorine production via membrane electrolysis. We allow for switching between two different operational modes with different respective electrical power demands on a per ton of produced chlorine ( $\text{Cl}_2$ ) basis and different modulation of production rate. Switching necessitates a cleaning procedure leading to downtimes of the  $\text{Cl}_2$  production, while a constant provision of  $\text{Cl}_2$  for downstream processes is necessary. The optimal operation of a variable and switchable chlor-alkali process under aforementioned constraints is determined by formulation as a mixed integer linear program. The results demonstrate that oversizing, in combination with switching, leads to substantial savings, especially in future scenarios for the electricity price. © 2018 American Institute of Chemical Engineers AIChE J, 65: e16352, 2019*

**Keywords:** chlor-alkali electrolysis, oxygen depolarized cathode, demand side management, demand response, MILP

## Introduction

The challenges of the future energy market arising by the increasing penetration of intermittently available renewable energy sources need to be considered by industry. A flexible operation that is adjustable to actual energy availability, so called demand side management (DSM), can be one strategy with which industrial processes can benefit economically from highly fluctuating energy availability and/or electricity prices. It simultaneously contributes to tackling the challenges of the future energy market by compensating parts of these high fluctuations.<sup>1</sup> In many publications, DSM with flexible plant operation is expected to be an important topic for energy-intensive chemical plants<sup>2,3</sup> and the benefits of DSM for different applications, for example, for the operation of a seawater reverse osmosis plant, have been shown.<sup>4</sup>

A promising candidate for flexibilization is the chlor-alkali process. The production capacity of chlor-alkali plants worldwide was 75 million metric tons of chlorine ( $\text{Cl}_2$ ) per year in 2017 according to the World Chlorine Council.<sup>5</sup> In Germany, the installed capacity of chlor-alkali electrolysis is 1.484 GW.<sup>6</sup> With an average electricity consumption of a  $\text{Cl}_2$  electrolysis

plant in 2010 of about 3.3 MWh per electrochemical unit (Electrochemical Unit (ECU) = product combination of 1 ton of  $\text{Cl}_2$ , 1.1 ton of caustic, and 0.03 ton of hydrogen [ $\text{H}_2$ ]), the chlor-alkali process is an energy-intensive process<sup>7</sup> revealing a high dependency of this sector on the energy market. Chlor-alkali electrolysis is used to produce the commodity chemicals  $\text{Cl}_2$  and sodium hydroxide (NaOH), as well as  $\text{H}_2$  from brine (NaCl and  $\text{H}_2\text{O}$ ). Chlorine is used in a variety of chemical processes, such as the production of polyvinyl chloride (PVC) or water treatment. Sodium hydroxide is used primarily in the pulp and paper, soaps and detergents, alumina, textile, and petroleum industries as a chemical intermediate. Due to the importance of  $\text{Cl}_2$  and NaOH for the chemical industry, the European industrial production of  $\text{Cl}_2$  was reported at 9578 kt/year for 2015.<sup>8</sup>

Usually, chlor-alkali processes are operated at high-capacity utilization to ensure maximum returns for this capital-intensive chemical process.<sup>9</sup> EuroChlor indicates an average capacity utilization rate of the European  $\text{Cl}_2$  production plants of 79.7%<sup>8</sup> for the year 2015. An already high utilization rate of the plants minimizes potentials for dynamic operation when load shifts between time periods are envisioned. Such load shifts typically are the basis for DSM. Besides, despite variable operation of the plant, a constant provision for downstream processes of the base chemical  $\text{Cl}_2$  or an intermediate product of downstream processes, such as ethylene dichloride (EDC), is necessary, making the storage of either of these products necessary. EDC can easily be stored, although, as it is only needed for the PVC

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production. For the remaining downstream processes,  $\text{Cl}_2$  is specifically required, making its storage necessary. As  $\text{Cl}_2$  is a hazardous substance, its storage is delicate. The size of the  $\text{Cl}_2$  storage tank is therefore limited, and should be as small as possible due to safety restrictions, making storage a limiting factor for variable  $\text{Cl}_2$  production.

A chlor-alkali process allowing different modes of operation (with the modes having different energy demands while keeping  $\text{Cl}_2$  production at the same level) can make DSM of this process lucrative, even with a limited  $\text{Cl}_2$  storage and an already high-capacity utilization of the plant. Typically, studies of DSM consider a variable production rate with buffering via storage. Here, mode switching to further enhance the economic benefit is added. This novel approach applied to the chlor-alkali electrolysis therefore combines the typical DSM by modulation of the production rate and a switching between two different operational modes with different electrical power demands per produced amount of  $\text{Cl}_2$ . This operation in different modes requires the technical ability to switch fast and efficiently between the modes for which minimal requirements are to be analyzed here. This flexible operation is only economically feasible if the savings due to flexible operation exceed the additional investment costs that are necessary for the flexible operation. Due to the required constant  $\text{Cl}_2$  provision for downstream processes, an oversized production plant is needed to compensate for the downtimes during cleaning intervals, such that fully capacity utilization will not be realized at all times. Furthermore, a process allowing different modes of operation must consider the different by-product production rates of the modes.

Optimization of such a switchable and variable plant operation falls under the concept of production scheduling. Scheduling problems are often very complex, making mathematical optimization necessary to ensure a profitable production with optimal capacity utilization.<sup>10</sup> Therefore, several publications from the last few decades address scheduling, the required formulation of mathematical models, as well as the development of algorithm architectures for solving such problems.<sup>11</sup>

In this study, the optimal operation of a chlor-alkali process that allows for different modes of operation is presented. A model for the bifunctional operation is set up and used in the optimization problem for minimizing the operating costs under fluctuating electricity prices while keeping the  $\text{Cl}_2$  provision for downstream processes constant. The operation of the chlor-alkali process is first optimized for fixed and stationary conditions to better assess the results of the subsequent optimization of a variable production. A combined variable and switchable operation is analyzed in the following. The calculated savings are evaluated by comparison to the necessary investment costs. In the end, a sensitivity study of the important process parameter of cleaning duration is conducted.

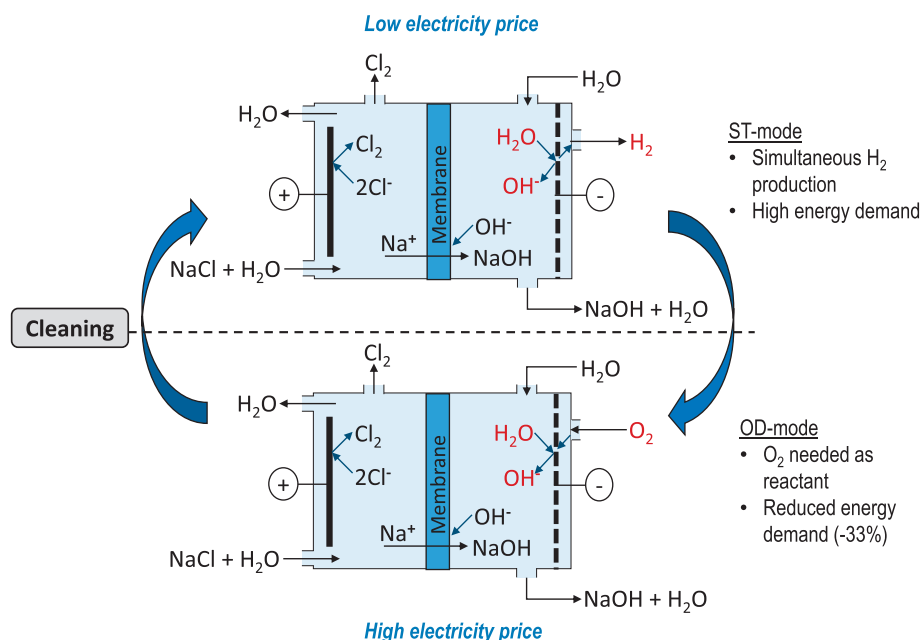
## Chlorine Production Strategies

Three variants of the chlor-alkali process exist in widespread commercial use, generally distinguished by how catholyte and anolyte are separated: diaphragm, amalgam, and membrane process. The chlorine production strategies presented in the following focus on the membrane process as it dominates modern installed capacity.<sup>8</sup> The strategies are the utilization of standard cathodes (STCs), oxygen depolarized cathodes (ODCs), and a bifunctional electrode, which can be used as both aforementioned cathodes depending on external conditions.

### Chlor-alkali electrolysis using STC

In a membrane cell, an ion-exchange membrane separates an anode and cathode compartment (Figure 1).

As described by Jung et al.,<sup>12</sup> the anode compartment is fed with saturated brine to produce  $\text{Cl}_2$  and sodium ions when a potential is applied. The sodium ions migrate through the membrane to the cathode compartment, where water is supplied. At the STC (see ST-mode in Figure 1), water is reduced to  $\text{H}_2$  and hydroxide ions. Together with the sodium ions, these hydroxide ions form  $\text{NaOH}$ . The minimal cell voltage for  $\text{Cl}_2$  production

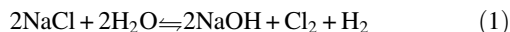


**Figure 1.** Illustration of the switching of a bifunctional electrode between the ST-mode and the OD-mode as well as the comparison of the design and operation of both modes.

[Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

with by-production of  $H_2$  at the STC is  $U_{\text{cell,min}} = 2.19 \text{ V}$  at standard conditions.<sup>13</sup> The operating voltage of a membrane cell including overpotentials occurring in a real electrochemical cell is  $U_{\text{cell,STC}} \approx 3.0 \text{ V}$  with a typical current density of  $4\text{--}6 \text{ kA/m}^2$ .<sup>14</sup>

Overall, the net reaction of the chlor-alkali electrolysis with the STC producing  $H_2$  as by-product is:



with the respective electricity demand at a typical operating point ( $U_{\text{cell,STC}} = 3 \text{ V}$ ,  $j_0 = 6 \text{ kA/m}^2$ ) for production of  $\text{Cl}_2$  in an electrolytic cell<sup>12</sup>:

$$W_{\text{El,STC}} = 2.338 \frac{\text{kWh}}{\text{kg}_{\text{Cl}_2}} \quad (2)$$

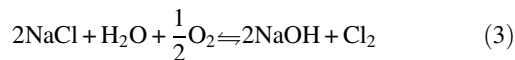
### Chlor-alkali electrolysis using ODC

The utilization of an ODC instead of the STC allows direct contact of the liquid electrolytic phase with a gas phase at the location of the catholytic electrochemical reaction. In the case of the chlor-alkali electrolysis, the direct contact of the cathodic liquid phase to gaseous oxygen ( $\text{O}_2$ ) enables the reduction of the theoretical cell voltage by  $1.23 \text{ V}$ . In practical applications, it can be expected that a reduction of potential of  $1.0 \text{ V}$  (due to higher overpotentials during  $\text{O}_2$  reduction) to  $U_{\text{cell,min}} \approx 2.0 \text{ V}$  can be reached.<sup>14</sup> A direct consequence of a lower cell potential is proportional energy savings. Compared to the membrane process using STC, the ODC-process, therefore, reduces the electricity demand by  $\sim 33\%$ .

ODCs have been known since at least 1950, when Butler suggested the application of this principle for the diaphragm process.<sup>15</sup> In 2011, a pilot plant using ODCs for chlor-alkali electrolysis (based on electrolysis of  $\text{NaCl}$ ) began operation.<sup>16</sup>

An electrolysis cell using an ODC is illustrated in Figure 1 (compare OD-mode). The anode compartment and the ion-exchange membrane are identical to the membrane process with the STC. In the cathode compartment, however, the ODC separates gaseous  $\text{O}_2$  and liquid  $\text{NaOH}$ . The ODC is designed to allow  $\text{O}_2$  diffusion into a reaction zone where the  $\text{O}_2$  reduction reaction can take place, while the ODC is withstanding the hydrostatic pressure of the liquid  $\text{NaOH}$ . In contrast to the membrane process using STCs,  $\text{O}_2$  is reduced at the ODC without  $\text{H}_2$  production.

The net reaction of the chlor-alkali electrolysis using an ODC is:



with the respective electricity demand at a typical operating point ( $U_{\text{cell,ODC}} = 2 \text{ V}$ ,  $j_0 = 6 \text{ kA/m}^2$ ) for production of  $\text{Cl}_2$  in an electrolytic cell<sup>12</sup>:

$$W_{\text{El,ODC}} = 1.558 \frac{\text{kWh}}{\text{kg}_{\text{Cl}_2}} \quad (4)$$

### Flexibilization of the chlor-alkali electrolysis

Both of the strategies for cathode operation presented above produce the same amount of  $\text{Cl}_2$  and  $\text{NaOH}$ , and use the same amount of sodium chloride ( $\text{NaCl}$ ). The major differences between both strategies are their differing specific electricity demand, the  $\text{H}_2$  production of the STC, and the  $\text{O}_2$  consumption of the ODC.

The flexibilization of the  $\text{Cl}_2$  production can now be achieved by a combination of two procedures. On the one hand, the process can be operated variably over time-with a reduced  $\text{Cl}_2$  production when electricity prices are high, and an elevated  $\text{Cl}_2$  production when electricity prices are low. On the other hand, both cathodic operation strategies (using the STC with  $\text{H}_2$  production and using the ODC with  $\text{O}_2$  consumption) can be combined in a bifunctional electrode. Preliminary experimental investigations performed by the authors demonstrate the possibility to operate a bifunctional cathode in both operating strategies,<sup>17</sup> producing  $\text{H}_2$  when no  $\text{O}_2$  is fed into the electrolyzer like an STC, here called ST-mode, or working as an ODC when  $\text{O}_2$  is provided to the cell, here called OD-mode. In the following, we therefore distinguish between three electrodes: the STC, the ODC, and the bifunctional electrode. The bifunctional electrode allows operation in the two different modes replacing either the STC or the ODC. The former mode replacing the STC is called ST-mode, the latter is called OD-mode. Such a bifunctional electrode provides the possibility to switch the operation of the electrolysis between both above-mentioned modes. Figure 1 shows such a switching procedure: When the electricity price is high, the process is being operated in the  $\text{O}_2$ -consumption mode (OD-mode) without  $\text{H}_2$  production, whereas when the electricity price is low, the process is being operated in the  $\text{H}_2$ -production mode (ST-mode) providing additional  $\text{H}_2$ .

As the electrode, which allows mode switching, has to be able to catalyze both electrochemical reactions, technical compromises in its design for both modes likely have to be made. This might lead to a higher electricity demand than for unique cell-operation with the respective electrode given in Eqs. 2 and 4. In this study, a best-case evaluation is intended and therefore the given electricity demands are used for the bifunctional electrode.

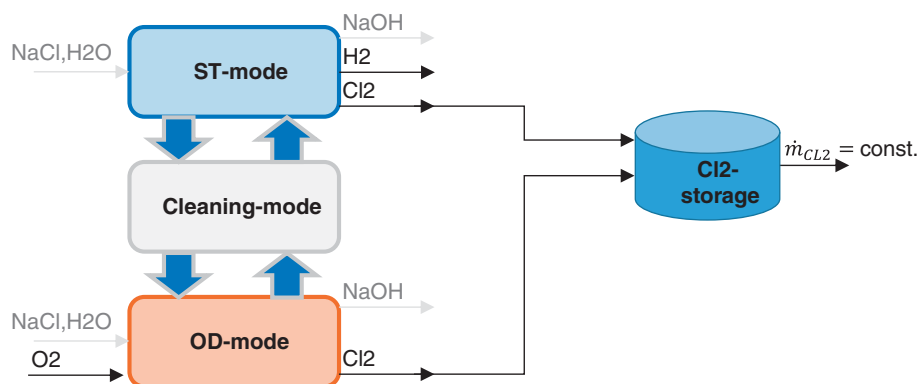
The challenge of this switchable operation is the fact that the molecules  $\text{H}_2$  and  $\text{O}_2$  have to be strictly separated to avoid the explosive oxidation. Therefore, a rinsing process removing  $\text{H}_2$  or  $\text{O}_2$  from the cell is necessary when switching from one operating mode to the other. This cleaning step causes downtimes of the  $\text{Cl}_2$  electrolysis. To guarantee a constant provision of the base chemical  $\text{Cl}_2$  for downstream processes (while having varying  $\text{Cl}_2$  production rates and even downtimes of the chlor-alkali electrolysis), a  $\text{Cl}_2$  storage tank, that for safety reasons must be of a minimal size, is required.

In addition,  $\text{Cl}_2$  is only one of the components being produced or used in the chlor-alkali electrolysis. All the other components are affected by a variable production as well, meaning that these other substances need to be stored alongside, during operating with DSM and it is necessary to presume that the temporary loss of  $\text{H}_2$  production can be met otherwise. As  $\text{H}_2$  is an important reactant for many chemical processes, this assumption strongly depends on the  $\text{H}_2$  storage infrastructure and the  $\text{H}_2$  demand at the specific site. In addition, the acquisition of  $\text{O}_2$  needs to be ensured for the switchable chlor-alkali electrolysis.

Figure 2 represents the complete scheme of the considered process with material flows, the reactive modes, a rinsing-mode, supplied reactant streams, by-product streams, and a storage tank for  $\text{Cl}_2$ .

### Model

The modeling of electrochemical cells has been widely studied, with a considerable number of models being available, ranging from empirical relationships to detailed descriptions of the physical and chemical processes in the various



**Figure 2.** Scheme representing the considered process setup for a switchable chlor-alkali electrolysis.

[Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

types of cells. Some models target parts of an electrochemical cell that are also relevant to chlor-alkali processes, for example, a model for an ion-selective membrane under conditions close to chlor-alkali electrolysis.<sup>18</sup> Some models are specifically applied to the chlor-alkali processes, for example, Chavan et al.<sup>19</sup> have deduced a one-dimensional (1-D) model of an industrial ODC cell for energy-efficient chlor-alkali electrolysis to calculate the distributions of temperature, concentration, current density, and overpotential along the height of the electrolyzer.

In the following section, a lumped, quasi-stationary model is presented. Time is discretized to  $n$  equidistant intervals, indexed by  $t$ .

### Modeling of transitional mode operation

For the implementation of a switchable operation, binary variables  $y$  are introduced for each mode  $m$  showing its (in) active status. The sum

$$\sum_m y_{m,t} = 1 \quad \forall t \in T$$

assures that only one of all modes  $m$  is active at each time point  $t$ . Here, four possible modes  $m \in \{\text{ST}, \text{OD}, \text{cleanSTOD}, \text{cleanODST}\}$  are considered with the reactive modes (ST, OD), and the cleaning modes (cleanSTOD, cleanODST). Modern mixed integer linear program (MILP) solvers, for example, CPLEX or Gurobi can efficiently deal with such SOS-1 sets.

A binary variable  $z_{mm',t}$  indicates whether there is a transition from mode  $m$  to mode  $m'$ . This binary transitional variable  $z_{mm',t}$  is true if and only if a transition from mode  $m$  to mode  $m'$  occurs from time  $(t-1)$  to time  $t$ . As shown by Mitra et al.,<sup>20</sup> these transition variables can be determined by the following constraint (when the self-transition variables  $z_{m,m}$  are not required).

$$\sum_{m'} z_{m',m,t-1} - \sum_{m'} z_{mm',t-1} = y_{m,t} - y_{m,t-1} \quad \forall m \in M, t \in T$$

Setting part of these variables to zero, for example,  $z_{m^1 m^2}$  suppresses the switching from mode  $m^1$  to mode  $m^2$ . Herein this is used to assure that a reactive mode does not directly follow the respective other reactive mode.

For all modes, a minimal duration of each mode is implemented: in the cleaning modes to guarantee complete gas removal and in the reactive modes to guarantee product quality and minimize material degradation.

To guarantee a minimal respective mode duration, the status of the mode in the preceding time steps is evaluated. The minimal mode duration  $\theta$  defines the number of preceding time steps to be considered. According to Zhang and Grossmann,<sup>21</sup> the constraint for minimal duration of one mode can be formulated by

$$y_{m',t} \geq \sum_{k=1}^{\theta_{mm'}} z_{mm',t-k} \quad \forall m, m' \in M, t \in T$$

where the plant has to stay in mode  $m'$  for at least  $\theta_{mm'}$  time periods after switching from mode  $m$  to mode  $m'$ .

### Process model

**Mass Balance.** Each reactive mode of the electrolysis plant  $m \in \{\text{ST}, \text{OD}\}$  is modeled via the above stated stoichiometric reactions (1) and (3) with proportional production and consumption rates  $\dot{m}_C$  of each component  $C$  as well as a mode-specific, rate-dependent electricity demand  $P_m$ . The production rates  $\dot{m}_{C,m}$  of each component in each reactive mode  $m$  have to be equal to zero if the respective mode is inactive (i.e., the respective binary variable representing its active and inactive status is  $y_m = 0$ ). The link between the continuous production rates and the binary variables  $y$  is realized using inequalities (5) forcing  $y_m$  to be equal to 1 if  $\dot{m}_{\text{Cl}_2,m}$  is greater than zero

$$\underline{\dot{m}}_{\text{Cl}_2,m} \cdot y_{m,t} \leq \dot{m}_{\text{Cl}_2,m,t} \leq \overline{\dot{m}}_{\text{Cl}_2,m} \cdot y_{m,t} \quad \forall m \in M, t \in T \quad (5)$$

with  $\underline{\dot{m}}_{\text{Cl}_2,m}$  being the lower bound and  $\overline{\dot{m}}_{\text{Cl}_2,m}$  the upper bound of  $\dot{m}_{\text{Cl}_2,m}$ . This corresponds to the BigM-formulation described by Williams<sup>22</sup>(p. 166ff). The total  $\text{Cl}_2$  production rate  $\dot{m}_{\text{Cl}_2,t}$  is determined as the sum of the  $\text{Cl}_2$  production rates in each mode  $\dot{m}_{\text{Cl}_2,m,t}$  even though only one mode can be active at a time.

**The cleaning mode comprises no consumption/production of elements but leads to downtimes of the  $\text{Cl}_2$  production during cleaning periods.**

**Chlorine Storage Tank.** The storage tank content is calculated via a mass balance of the storage content  $m_{\text{SCL}_2}$  under the condition that the content stays within its lower and upper bounds  $\underline{S}_{\text{Cl}_2}$  and  $\overline{S}_{\text{Cl}_2}$ , where  $S_{\text{Cl}_2,t}$  is the backup time of the storage calculated by division of the current storage content ( $m_{\text{SCL}_2,t}$ ) by the normalized downstream need of  $\text{Cl}_2$  ( $\dot{m}_{\text{N,Cl}_2}$ ):

$$S_{\text{Cl}_2,t} = \frac{m_{\text{SCL}_2,t}}{\dot{m}_{\text{N,Cl}_2}}.$$

This backup time  $S_{Cl_2,t}$  represents the time that can be bridged by the  $Cl_2$  tank to satisfy the downstream  $Cl_2$  demand during downtimes of the chlor-alkali electrolysis.

Due to the required constant  $Cl_2$  provision for downstream processes, the total amount of  $Cl_2$  produced in the considered time horizon has to remain the same for every possible operating strategy, independent of the time at which this amount is produced. This is guaranteed by a fixed downstream need for  $Cl_2$  taken out of the  $Cl_2$  storage tank at each time point  $t$ , and an end-point constraint that sets the  $Cl_2$ -storage content to the same level as at the beginning of the considered time horizon. Thus, the total produced amount of  $Cl_2$  is fixed in the optimization.

### Electricity demand of the cell

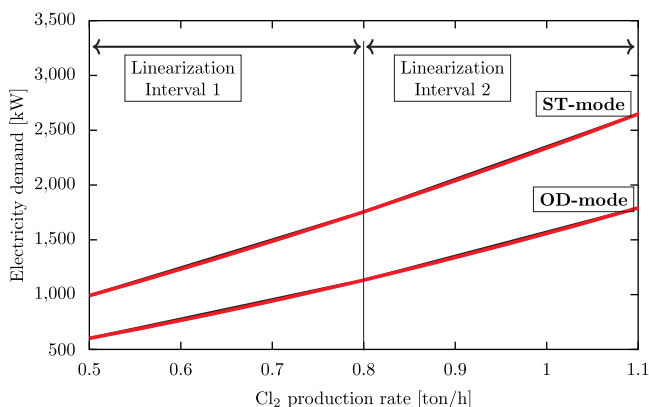
A specific  $Cl_2$  production necessitates a specific electricity provision. Given a plant capacity  $\dot{m}_{N,Cl_2} = 1t_{Cl_2}/h$ , with the specific electricity demands of both modes at a typical current density of 6 kA/m<sup>2</sup> provided above, the electricity demand of the plant can be deduced (Supporting Information Section S1), and is shown in Figure 3 as a function of the  $Cl_2$  production rate ( $\dot{m}_{Cl_2,t}$ ).

In the implementation, the actual electrical power demand is calculated *via*:

$$P_t = P_{ST,t} + P_{OD,t} = \sum_i P_{m,t} \quad \forall t \in T$$

to determine an overall electricity demand  $P_t$  as the sum of the individual electricity demands of all reactive modes  $m \in \{ST, OD\}$ , given that only one of the modes is active (the cleaning modes have no electricity demand). For the calculation of the variable electricity demands of each mode (depending on the actual production rate), the almost-linear functions in Figure 3 are approximated by a piecewise-linear function to keep an MILP-formulation while keeping the error of the estimated electricity demand low.  $P_{m,t}$  therefore denotes the electrical power consumption of each mode  $m$  with respect to its (in) activity. It is calculated *via*:

$$P_{m,t} = \sum_e \left( k_{m,e,t} \cdot b_{m,e} + a_{m,e} \cdot \dot{m}_{lin,Cl_2,m,e,t} \cdot \frac{3600 \text{ s}}{1 \text{ h}} \right) \quad \forall m \in M, t \in T$$



**Figure 3. Assumed electricity demand subject to the produced amount of  $Cl_2$  for both modes (red) and the respective regression curves (black).**  
[Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

with the y-axis interception  $b_{m,e}$  and the gradient  $a_{m,e}$  of each mode  $m$  and each interval  $e$  of the piecewise-linear functions in Figure 3.  $k_{m,e,t}$  indicates whether an interval  $e$  of the linearized electricity demand of a mode  $m$  is active at time  $t$ . It therefore has to comply with the condition that the sum of all  $k$  over all intervals  $e$  of one mode  $m$  must be equal to the binary variable  $y_{m,t}$ , indicating the (in)active status of that mode  $m$  *via*:

$$\sum_e k_{m,e,t} = y_{m,t} \quad \forall m \in M, t \in T.$$

$\dot{m}_{lin,Cl_2,m,e,t}$  is the  $Cl_2$  production in interval  $e$  and equal to the actual  $Cl_2$  production when the corresponding mode  $m$  is active and when the  $Cl_2$  production is within the bounds  $\underline{\dot{m}}_{Cl_2,e}, \bar{\dot{m}}_{Cl_2,e}$  of the corresponding interval  $e$ .  $\dot{m}_{lin,Cl_2,m,e,t}$  is calculated by the following constraints:

$$\begin{aligned} \dot{m}_{lin,m,e,t} &\leq \bar{\dot{m}}_{Cl_2,e} \cdot k_{m,e,t} & \forall m \in M, e \in E, t \in T \\ \dot{m}_{lin,m,e,t} &\geq \underline{\dot{m}}_{Cl_2,e} \cdot k_{m,e,t} & \forall m \in M, e \in E, t \in T \\ \sum_e \sum_m \dot{m}_{lin,m,e,t} &= \dot{m}_{Cl_2,t} & \forall t \in T \end{aligned}$$

### Ramping constraints

When envisaging a change in the production rate of the real plant, a certain time is needed to ramp the production from one operating level to another. This is included in the model to avoid unrealistic fast changes of the production rates. Therefore, in the model, the increase of the production rate from time point ( $t$ ) to the subsequent time point ( $t + 1$ ) is limited based on a maximal allowable production increase/decrease  $\Delta \dot{m}_{Cl_2}$  per time step which is calculated *via*

$$\Delta \dot{m}_{Cl_2} = \frac{\bar{\dot{m}}_{Cl_2} - \underline{\dot{m}}_{Cl_2}}{\theta_{ramp} \cdot \Delta t}$$

depending on the number of time steps  $\theta_{ramp}$  that are necessary to ramp the production between the maximal and minimal active reaction rates  $\bar{\dot{m}}_{Cl_2}$  and  $\underline{\dot{m}}_{Cl_2}$ . The maximal and minimal allowable production rate of the subsequent time step ( $t + 1$ ) therefore depends *via*:

$$\begin{aligned} \dot{m}_{Cl_2,t+1} &\leq \dot{m}_{Cl_2,t} + \sum_m y_{m,t} \cdot \Delta \dot{m}_{Cl_2} \cdot \Delta t + \left( 1 - \sum_m y_{m,t} \right) \cdot \underline{\dot{m}}_{Cl_2} \\ \forall m &\in \{ST, OD\}, t \in T / \{t_n\} \end{aligned} \quad (6)$$

$$\begin{aligned} \dot{m}_{Cl_2,t+1} &\geq \dot{m}_{Cl_2,t} - \sum_m y_{m,t+1} \cdot \Delta \dot{m}_{Cl_2} \cdot \Delta t - \left( 1 - \sum_m y_{m,t+1} \right) \cdot \underline{\dot{m}}_{Cl_2} \\ \forall m &\in \{ST, OD\}, t \in T / \{t_n\} \end{aligned} \quad (7)$$

$$\begin{aligned} \dot{m}_{Cl_2,t} &\geq \sum_m y_{m,t} \cdot \underline{\dot{m}}_{Cl_2} \\ \forall m &\in \{ST, OD\}, t \in T \end{aligned} \quad (8)$$

on the value of the production rate in the current time step ( $t$ ) plus/minus  $\Delta \dot{m}_{Cl_2}$  if one of the reactive modes  $m \in \{ST, OD\}$  is active, see Eqs. (6) and (7). This also applies to mode switches. Here, the plant always has to be ramped to  $\underline{\dot{m}}_{Cl_2}$  before it can be switched to the other reactive mode. A reaction rate below  $\underline{\dot{m}}_{Cl_2}$  is only allowed at  $\dot{m}_{Cl_2} = 0$  when none of the reactive modes are active (8). If none of the reactive modes are active in time step ( $t$ ), the production rate  $\dot{m}_{Cl_2}$  of the subsequent time step ( $t + 1$ ) is limited to the values  $\underline{\dot{m}}_{Cl_2}$  or 0.



## Objective function

The goal of this study is to find the optimal operation of a chlor-alkali process. It is determined whether operation with an STC, an ODC or a bifunctional cathode allowing switching from the ST-mode to the OD-mode (under condition of cleaning between both modes) is optimal under consideration of fluctuating electricity prices. The conditions, making switching of the bifunctional electrode from one mode to the other possible and profitable, are revealed. In the optimization, the operation of the STC is equal to the operation of the bifunctional electrode solely in the ST-mode, the operation of the ODC is equal to the operation of the bifunctional electrode solely in the OD-mode. Optimal operation is reached when the operating costs are minimized, provided that the production rates remain the same. The operating costs of each mode can be calculated by the expenses for each operating material, considering the stoichiometric consumption and production, and the electricity demand for each mode:

$$\begin{aligned}\text{Expenses}_{\text{ST}} &= C_{\text{NaCl,ST}} + C_{\text{El,ST}} \\ \text{Expenses}_{\text{OD}} &= C_{\text{NaCl,OD}} + C_{\text{El,OD}} + C_{\text{O}_2,\text{OD}} + C_{\text{H}_2,\text{ST}}\end{aligned}$$

with the costs  $C_C$  for each component  $C$ .  $\text{H}_2$  is taken into account as an operating cost in the OD-mode as it is usually provided by the ST-mode for downstream processes and therefore has to be purchased when not produced by the chlor-alkali electrolysis to still meet the demand. By doing so, only the reactants of both reactive modes differ, but the products and their production rates are the same and can therefore be neglected in the analysis of the switching. The difference in water utilization is neglected as water is assumed to have low costs and therefore only little impact on the expenses.

Decisive for the decision whether one or the other mode is more beneficial for the operation is the difference between the operating costs of both modes. The operating costs of the plant  $\Delta\text{Expenses}$  are equal to the Expenses for the currently active mode. The objective function therefore needs to evaluate  $\Delta\text{Expenses}$  at each discretized time point of the considered time horizon to estimate the lowest possible sum of Expenses for the whole interval:

$$\min_{\dot{m}_{\text{Cl}_2}, y} \sum_{t=0}^{t_n} \Delta\text{Expenses}_t$$

$$\Delta\text{Expenses}_t = \text{Expenses}_{\text{ST},t} \cdot y_{\text{ST},t} + \text{Expenses}_{\text{OD},t} \cdot y_{\text{OD},t}$$

The purchase of NaCl is not decisive in  $\Delta\text{Expenses}$ , as the consumption of this substance per produced ton  $\text{Cl}_2$  is the same in both reactive modes and therefore not relevant for the decision of the optimal mode. Although as the costs for NaCl are not negligible when evaluating a potential decrease of operational costs, the costs for NaCl are considered in  $\Delta\text{Expenses}$ .

The costs  $C$  are calculated by the specific prices  $p$  (constant for the components, time-variable for electricity) multiplied by the respective consumption  $\dot{m}_C$  for the mass flows or  $P$  for the electricity consumption and the time step  $\Delta t$ :

$$\begin{aligned}C_{C,t} &= p_C \cdot \dot{m}_{C,t} \cdot \Delta t \quad \forall t \in T \\ C_{\text{El},t} &= p_{\text{El},t} \cdot P_t \cdot \Delta t \cdot \frac{1 \text{ h}}{3600 \text{ s}} \quad \forall t \in T.\end{aligned}$$

## Model summary

The quasi-stationary model consists of 24 binary and 38 continuous variables per discretization interval. Considering 1 week

discretized by intervals of 10 min, the model consists of a total of 62,496 variables.

## Prices

For the evaluation of the objective function, the specific prices of the commodities considered in that function need to be given.

**Typical prices for  $\text{H}_2$ ,  $\text{O}_2$ , and NaCl** **Hydrogen.** The production costs for  $\text{H}_2$  produced from coal and natural gas is in the range of 0.36–1.83 \$/kg and 2.48–3.17 \$/kg, respectively.<sup>23</sup> Grube et al. state values for  $\text{H}_2$  production costs in the range of €1.5/kg for  $\text{H}_2$  production based on natural steam-reforming, up to €5.9/kg for  $\text{H}_2$  production via electrolysis by wind energy, or even €9.5/kg for electrolysis by solar energy.<sup>24</sup> The cheapest mentioned method of production therefore is steam reforming. Assuming a production cost of €1.5/kg for  $\text{H}_2$  production, the valorization prize has to be slightly higher. Here, a purchase price for  $\text{H}_2$  of

$$p_{\text{H}_2} = 2\text{€}/\text{kg}$$

is assumed.

**Oxygen.** The price for  $\text{O}_2$  varies substantially depending on the market in which it is sold, the scale of production and its level of quality (purity).<sup>25</sup> Ebrahimi et al. consider  $\text{O}_2$  prices of 50 \$/ton.<sup>25,26</sup> Hugill et al. set the  $\text{O}_2$  price to €68/ton for their calculations<sup>27</sup> and Gassner and Maréchal to €70/ton.<sup>28</sup> In his dissertation study, Sterner uses an  $\text{O}_2$  price of €70/ton.<sup>29</sup> Here, the price for  $\text{O}_2$  is assumed at

$$p_{\text{O}_2} = 0.05\text{€}/\text{kg}.$$

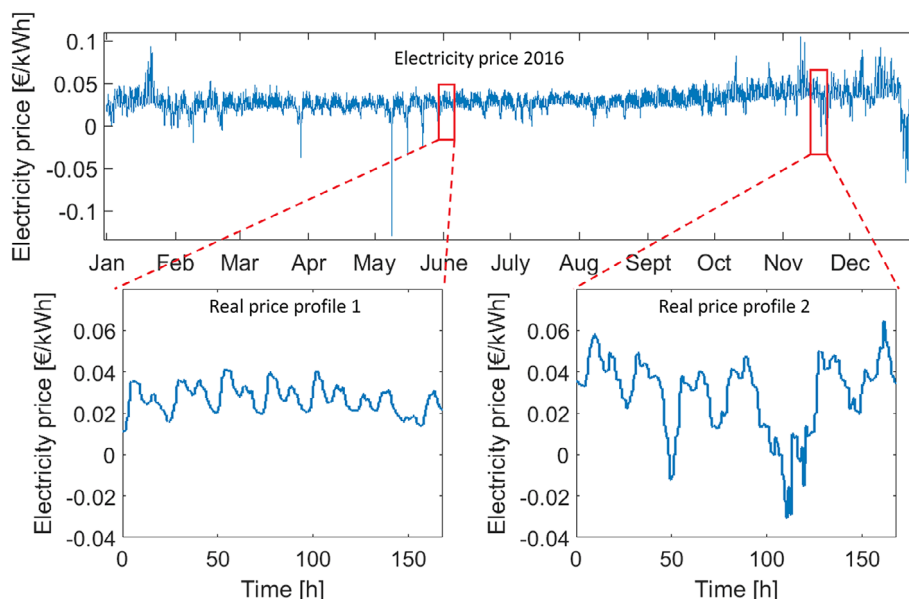
**Sodium chloride.** The price for NaCl is assumed at

$$p_{\text{NaCl}} = 0.04\text{€}/\text{kg}.$$

**Electricity Price.** Electricity in big volumes is traded at the spot market of the German EPEX electricity exchange. Therefore, the prices are determined one day ahead for every hour of the following day based on demand and predicted supply.<sup>30</sup>

Herein, different price profiles with the duration of one week are analyzed. Figure 4 shows the development of the electricity price at the German EPEX electricity exchange over the course of the year 2016 and enlarges the prices during two weeks of that year. The first enlarged profile shows the development of the electricity price during one week in June which is representative for a typical week in that year. The second shows the electricity price during one week in November with higher fluctuations. These electricity price profiles will be used as a basis for calculating the optimal operation of a chlor-alkali electrolysis with a variable production rate.

**Electricity Price Outlook.** In the future, electricity prices different from the above presented profiles of 2016 are expected. In 2016, a total of 648.4 TWh electricity was generated of which 188.2 TWh originated from renewable energy sources such as wind, water, biomass, or photovoltaics.<sup>31</sup> The availability of these renewable energy sources is weather-dependent and therefore varies over time. An increasing employment of renewable energy sources will lead to increasing fluctuations in electricity availability and therefore increasing electricity price fluctuations. In addition, a higher average price of electricity is probable due to higher leveled costs of electricity from renewable energy sources than from fossil fuels or nuclear power.<sup>32</sup>



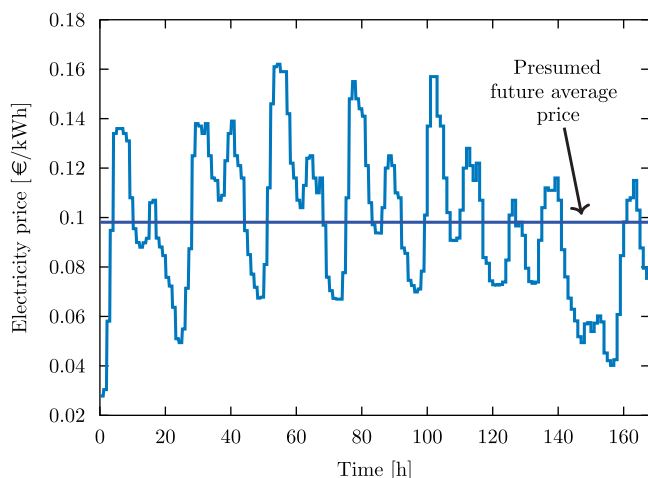
**Figure 4. Electricity prices in 2016 (data taken from: Agora Energiewende<sup>30</sup>).**  
[Color figure can be viewed at wileyonlinelibrary.com]

Given the considerations in the Supporting Information (Section 2), the future price profile shown in Figure 5 is generated and analyzed in the optimization. In that future price profile, it is assumed that the fluctuations (= the deviations from the average price) are three times as high as in 2016 around a higher average price of 0.0981 €/kWh.

## Optimization

The optimization of the presented MILP is conducted in General Algebraic Modeling System (GAMS 24.9.1) with CPLEX12 for different scenarios.

To better assess the results of the subsequent optimization and to reveal the impact of fluctuating electricity prices and time-dependent operation with downtimes for plant cleaning, the process is analyzed for fixed and stationary conditions first. An evaluation of a variable production rate is then given. In the end, a combined variable and switchable operation is analyzed for the future electricity price profile.



**Figure 5. Herein considered future electricity price profile.**  
[Color figure can be viewed at wileyonlinelibrary.com]

## Steady-state analysis

In this section, the impact of fixed prices on the choice of the optimal mode is analyzed and reveals the respective profitable mode under changing conditions of prices for reactants and electricity. Therefore, the electricity price, where both processes are economically equal, here called break-even price, is calculated.

The condition leading to a preference of operation in the ST-mode is less operating costs in the ST-mode than in the OD-mode:

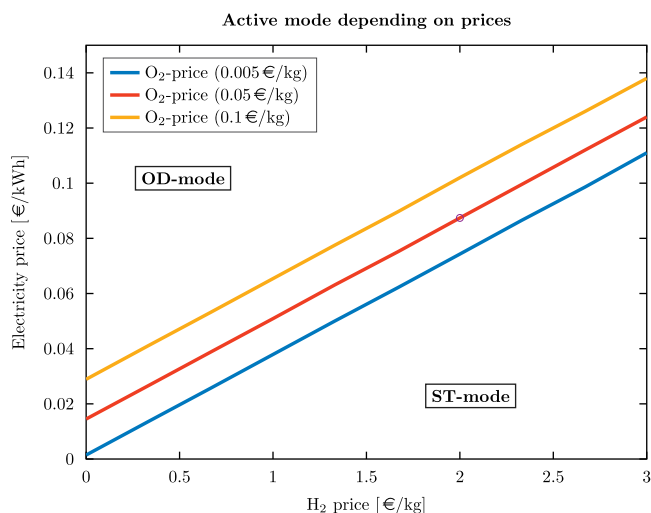
$$\text{Expenses}_{\text{ST}} \leq \text{Expenses}_{\text{OD}}.$$

Normalization of the production to 1 ton  $\text{Cl}_2$  per hour and conversion of the stoichiometric reaction rates to mass flows with the molar masses  $M_C$  of the respective component  $C$  ( $M_{\text{Cl}_2} = 70.9 \text{ g/mol}$ ,  $M_{\text{H}_2} = 2.02 \text{ g/mol}$ ,  $M_{\text{O}_2} = 32 \text{ g/mol}$ ) leads to the evaluation of the inequality

$$0.028 \frac{\text{kg}_{\text{H}_2}}{\text{kg}_{\text{Cl}_2}} \cdot p_{\text{H}_2} + 0.226 \frac{\text{kg}_{\text{O}_2}}{\text{kg}_{\text{Cl}_2}} \cdot p_{\text{O}_2} \geq 0.780 \frac{\text{kWh}}{\text{kg}_{\text{Cl}_2}} \cdot p_{\text{El}}. \quad (9)$$

The sensitivity of Eq. 9 with respect to the prices can be determined to  $S_{\text{H}_2} = 0.028 \frac{\text{kg}_{\text{H}_2}}{\text{kg}_{\text{Cl}_2}}$ ,  $S_{\text{O}_2} = 0.226 \frac{\text{kg}_{\text{O}_2}}{\text{kg}_{\text{Cl}_2}}$ , and  $S_{\text{El}} = 0.780 \frac{\text{kWh}}{\text{kg}_{\text{Cl}_2}}$ . These sensitivities show that changes in the  $\text{O}_2$  price have a larger impact on the break-even price than changes in the  $\text{H}_2$  price.

For typical prices (given in section “Typical prices for  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{NaCl}$ ”), the relationship of when it is beneficial to operate in which mode can be plotted (Figure 6). The lines in the plot represent the break-even price where both modes yield the same operational costs. The circle in the plot shows that with the herein assumed typical prices, that is, with a typical  $\text{O}_2$  price of €0.050/kg and a typical  $\text{H}_2$  price of €2/kg, the break-even electricity price is €0.0874/kWh. **Electricity prices above this value induce operation in the OD-mode and electricity prices below this value induce operation in the ST-mode.** These results indicate that the operation mainly depends on site- or regional-specific conditions, such as provision of  $\text{O}_2$  and  $\text{H}_2$  with the locally given prices.



**Figure 6. Break-even prices where both modes yield the same operational costs.**

The circle represents the break-even electricity price of € 0.0874/kWh for typical H<sub>2</sub> and O<sub>2</sub> prices. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

The operating cost distribution for the above-mentioned specific component costs and an electricity price at the break-even price for both respective modes is compared in Table 1 for 1 h of plant operation to produce 1 ton of Cl<sub>2</sub>. Although the costs for electricity are much lower in the OD-mode, the additional costs for O<sub>2</sub> and H<sub>2</sub> level out this effect so that the total operating costs are the same in both modes.

For typical H<sub>2</sub> and O<sub>2</sub> prices, the ST-mode with by-production of H<sub>2</sub> in the chlor-alkali electrolysis is beneficial for a large range of electricity prices (under the assumption of a constant Cl<sub>2</sub> demand of downstream processes). Given the average electricity price in Germany in 2016 of €0.029/kWh, operation in the ST-mode was more beneficial in 2016 (Figure 6). The electricity price in Germany in 2016 was higher than the break-even price during only 5 h of that year.

If H<sub>2</sub> prices differ from the herein assumed typical H<sub>2</sub> price, the break-even price would differ from the break-even price presented above. For example, assuming no need of H<sub>2</sub> close to the chlor-alkali plant, a resulting H<sub>2</sub> price of €0/kg would lead to a significantly lower break-even price and would favor the OD-mode.

### Optimization of variable and switchable production

Evaluation of the operation under fixed conditions (“Steady-state analysis” section) reveals the break-even electricity price dictating the beneficial mode when reactant prices are kept constant. However, electricity prices are particularly highly fluctuating due to fluctuating electricity availability (caused by an increasing amount of intermittent renewable energy sources). Large fluctuations in the actual electricity price

**Table 1. Cost Distribution for Both Modes per Hour of Constant Cl<sub>2</sub> Production at the Break-even Electricity Price of €0.0874/kWh**

	ST-mode	OD-mode
Electricity (€/h)	206	137.8
NaCl (€/h)	65.9	65.9
H <sub>2</sub> (€/h)	0	56.9
O <sub>2</sub> (€/h)	0	11.3
Total	271.9	271.9

suggest that a variable Cl<sub>2</sub> production rate might be promising. Furthermore, the expected increase in the fluctuations of the future electricity price encourages this presumption.

As electricity production from renewable energy sources is envisaged to increase in the future, higher average electricity prices are also probable. Combined with higher fluctuations, the higher average price may cause that the electricity price passes the break-even price more often in the future. Using a bifunctional cathode that allows the operation in both aforementioned modes enables a mode switching between both operating strategies, with mode activation depending on the electricity price. Therefore, the flexibilization of the Cl<sub>2</sub> production can be achieved by a combination of a dynamic operation (*via* variable production rates) and switching between the ST-mode when electricity prices are low (due to higher electricity demand for additional H<sub>2</sub> production) or the OD-mode when electricity prices are high (with lower electricity demand, but the same Cl<sub>2</sub> production). However, these modes cannot be switched between one another directly as it is important to remove O<sub>2</sub> (or H<sub>2</sub>) completely from the reactor before switching to the respective other mode to strictly avoid the mutual contact of these gases. This implies the need for a cleaning step.

The following section takes a closer look at the benefit of a variable operation of a production plant that has been oversized by 10%, considering time-dependent changes in the electricity price for real price profiles of 2016 (refer to “Electricity price” section). Here, the objective function is evaluated for steady-state operation and for variable operation to compare the performance of both operating strategies. Subsequently, a probable electricity price profile representing future price constellations (presented in Figure 5) and their influence on a variable and switchable Cl<sub>2</sub> production is analyzed.

Both analyses are realized with the above-mentioned quasi-stationary model and discretized time where the production rate  $\dot{m}_{\text{Cl}_2}$  and the active mode (represented by  $y_m$ ) can be varied and therefore are control variables at each time point  $t$ . A variable production rate varies the amount of produced Cl<sub>2</sub>, and therefore the conversion of the stoichiometric reactions shown in the “Chlor-alkali electrolysis using STC” section and the “Chlor-alkali electrolysis using ODC” section.

### Additional assumptions

The following assumptions are used for the optimization.

- The considered time horizon is 1 week and is discretized to time intervals of  $\Delta t = 10$  min.
- The Cl<sub>2</sub> production is normalized to a production of  $\dot{m}_{\text{N,Cl}_2} = 1 \text{ t}_{\text{Cl}_2}/\text{h}$ . Therefore, this amount is continuously taken out of the Cl<sub>2</sub> storage tank.
- The Cl<sub>2</sub> production plant is oversized by 10% so that the maximum possible production capacity of the herein considered electrolyzer is  $\bar{\dot{m}}_{\text{Cl}_2} = 1.1 \dot{m}_{\text{N,Cl}_2}$ .
- The minimal possible production capacity still satisfying product quality requirements is 50% of maximal capacity:  $\underline{\dot{m}}_{\text{Cl}_2} = 0.5 \bar{\dot{m}}_{\text{Cl}_2}$ .
- Variations in the production rate cannot be instantaneous. It is assumed that ramping the production from  $\underline{\dot{m}}_{\text{Cl}_2}$  to  $\bar{\dot{m}}_{\text{Cl}_2}$  takes 30 min leading to  $\theta_{\text{ramp}} = 3$ . Other changes in the operating level are proportional to this duration.
- The production can only be switched to the cleaning mode when the production rate is at its nonzero minimum  $\underline{\dot{m}}_{\text{Cl}_2}$ .



- g. The initial backup time of the  $\text{Cl}_2$  storage tank is assumed to satisfy a downstream  $\text{Cl}_2$  demand of 1 h via  $S_{\text{Cl}_2, t=0} = 1 \text{ h} = S_{\text{Cl}_2, t_n}$ .
- h. The bounds of the backup time of the  $\text{Cl}_2$  storage tank are  $\underline{S}_{\text{Cl}_2} = 0 \text{ h}$  and  $\bar{S}_{\text{Cl}_2} = 3 \text{ h}$ .
- i. After switching, the newly activated mode is presumed to be active for at least 6 h to prevent the whole production unit, especially the electrodes and the sensitive membranes, from damage due to numerous switching:  $\theta_{\text{clean,ST}} = 36 = \theta_{\text{clean,OD}}$ .
- j. The duration of the necessary cleaning steps is based on estimation. The assumed values for the modes cleanSTOD and cleanODST are chosen to be 10 min:  $\theta_{\text{OD,clean}} = \theta_{\text{ST,clean}} = 1$ . These parameters need to be experimentally determined in the future.
- k. To conduct a best-case optimization, cleaning costs are neglected. (Only the penalty due to downtime of the  $\text{Cl}_2$  production is considered.)
- l. Capital costs are not considered.

### Results for variable operation

As the electricity price for the considered price profiles of 2016 is below the break-even price, operation in the ST-mode is more beneficial during the whole considered week. Therefore, the variable operation of a cell with a STC for price profiles 1 and 2 is presented in Figure 7. It clearly shows how the operation is varied over time by a varying  $\text{Cl}_2$  production in the chlor-alkali electrolysis. Whenever the electricity price shows a downwards trend, the  $\text{Cl}_2$  conversion is ramped to high conversion rates and the  $\text{Cl}_2$  storage tank content increases. When the electricity price is high, the conversion rate is low or even at its minimal value depending on the  $\text{Cl}_2$  storage content.

Compared to a stationary operation with an STC (see the bar chart in Figure 8), the stationary operation with an ODC

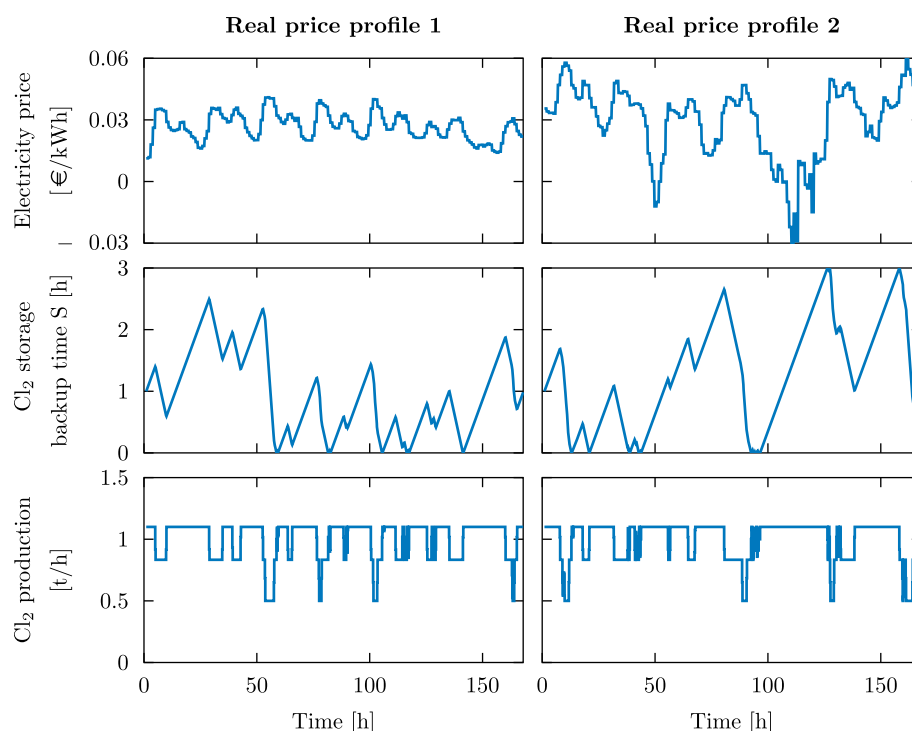
reduces the electricity costs by ~33% for both price profiles but increases the total costs by 36.5% in price profile 1 and by 33.7% in price profile 2 due to the additional costs of  $\text{O}_2$  and  $\text{H}_2$ . A variable operation with an STC reduces the electricity costs during 1 week of variable operation by 3.4% when having produced the same total amount of  $\text{Cl}_2$  after 1 week, but adjusting the electricity consumption to the electricity price under the aforementioned constraints. The total operating costs can be reduced by 1.6%. Optimal variable operation with an STC of real price profile 2 leads to electricity cost savings of 7.1% and total operating cost savings of 3.6%.

### Results for switchable operation

For the real price profiles of 2016, switching between the modes is not beneficial, as the break-even price is never reached. However, it is of great interest whether a switchable operation might become beneficial in the future. Therefore, an optimization of plant operation for the future price profile (Figure 5) is conducted where the proposed mean electricity price of 0.0981€/kWh is higher than the break-even electricity price of 0.0874€/kWh, meaning that here, primarily operation in the OD-mode is beneficial. However, temporarily switching to the ST-mode might be beneficial, if the electricity price decreases to a value below the mentioned break-even price for a time period that is long enough to make switching profitable.

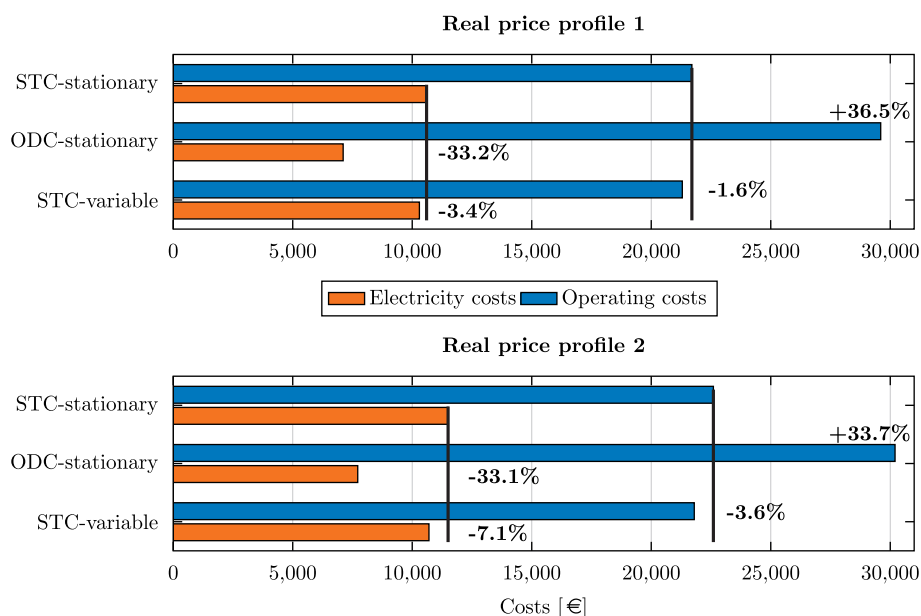
Figure 9 presents the optimal operation of a bifunctional electrode during the considered time horizon (left column) and enlarges the first 12 h of the considered time horizon (right column) to focus on the correlation of electricity price (in the first row), the modes (in the second row), the  $\text{Cl}_2$  storage content (in the third row) and the  $\text{Cl}_2$  conversion rate (in the fourth row).

Observing the first 12 h, operation starts in the ST-mode. When the electricity price increases to high values, the



**Figure 7.** Variable operation for the real electricity price profiles 1 and 2 with the course of the electricity price profiles in the first row, the content of the  $\text{Cl}_2$  tank in the second row and the  $\text{Cl}_2$  production rate in the third row.

[Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]



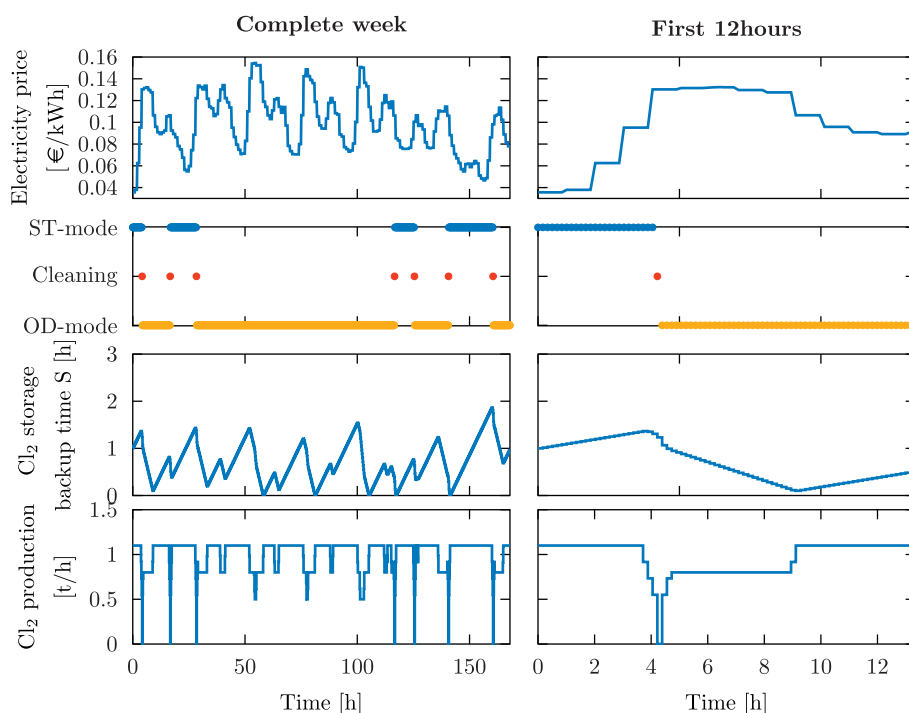
**Figure 8. Electricity cost savings and total operating cost savings compared to stationary operation of a chlor-alkali electrolysis with an STC for the real electricity price profiles 1 and 2.**

[Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

production rate is decreased by ramping down the production until it reaches 50% capacity utilization. Immediately, the plant is switched *via* the cleaning mode to the OD-mode where it is operated at a lower than maximal production rate until the electricity price decreases again. Then, when the electricity price decreases, the plant operation is turned back to maximal capacity utilization ( $\bar{m}_{Cl_2}$ ) to meet the downstream  $Cl_2$  demand as well as refilling the  $Cl_2$  storage tank.

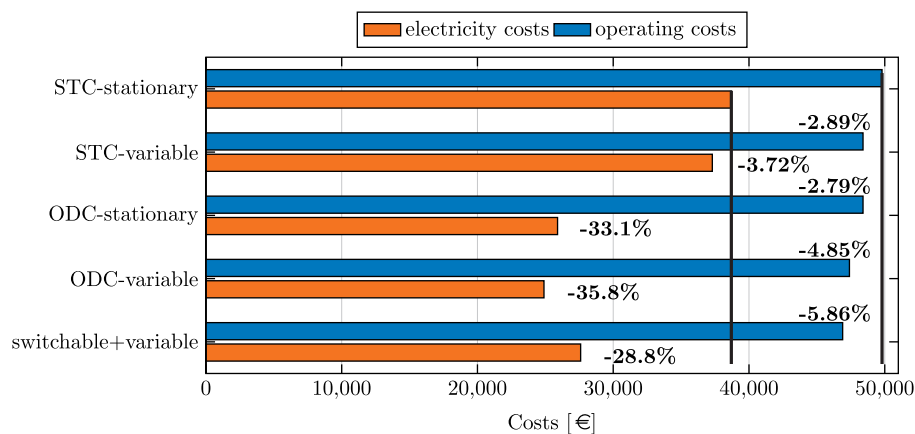
According to the results, when a bifunctional electrode with variable plant operation is used, the plant is mainly to be operated in the OD-mode for the future price profile with a total downtime of the  $Cl_2$  production plant of 50 min. This downtime is needed for cleaning with cleaning intervals of 10 min.

Compared to the stationary operation with an STC, the variable operation of this cathode decreases both electricity costs and operating costs (see the bar chart in Figure 10). The



**Figure 9. Switchable and variable operation for the future electricity price profile.**

The first row presents the electricity price, the second row shows which mode is active at which time-step, the third row presents the content of the  $Cl_2$  storage tank and the fourth row presents the  $Cl_2$  production rate. The left column presents the results of the whole considered time horizon. The right column shows the optimal operation during the first 12 h of the time horizon. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]



**Figure 10. Electricity cost savings and total operating cost savings compared to stationary operation of a chlor-alkali electrolysis with an STC for the future electricity price profile.**

[Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

stationary operation of an ODC reduces the electricity consumption by 33.1% due to the lower electricity demand of operation with this cathode and the total operating costs by 2.79%. Further increases can be obtained when the ODC is operated with a variable production rate. This saves 35.8% of the electricity costs and 4.85% operating costs compared to the stationary operation with an STC. As the STC is the standard in most plants, the plant would have to be fitted with new electrodes for operation with the ODC. The utilization of the bifunctional electrode requires a changeover of the plant as well, but combines the advantages of both modes. Although the bifunctional electrode leads to less electricity cost savings (28.8%) than the variable operation of the ODC, the highest reduction in total operating costs can be reached (5.86% compared to the stationary operation with an STC).

The herein assumed price for  $H_2$  of €2/kg is substantially lower than typical prices for  $H_2$  directly produced from renewable energy sources which according to Grube et al. range from €3/kg for  $H_2$  production *via* electrolysis by wind energy, up to even €9.5/kg for electrolysis by solar energy.<sup>24</sup> As shown in Figure 9, there are several times at which  $H_2$  is coproduced in the switchable chlor-alkali electrolysis. This implies that the coproduction is price competitive compared to production in an electrolysis plant dedicated solely for  $H_2$  production. A potential reason is that no equipment remains idle, as dedicated  $H_2$  production plants based on renewable would. A disadvantage of the coproduction in that respect is that the  $H_2$  production is at most equal to the  $Cl_2$  production.

In an economy fueled only by renewable energy, likely the  $H_2$  price will increase substantially. This would favor the ST-

mode over the OD-mode, possibly to the extent of no switching, as analyzed in Figure 6.

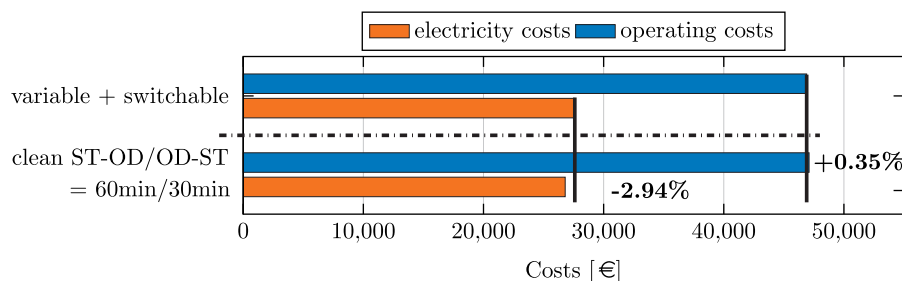
### Return on investment

The calculated savings need to be evaluated by comparison to the necessary investments. Presumed, as a basis for the calculation of the investment costs is a chlor-alkali electrolysis plant that is equipped with today's standard cathode for  $Cl_2$  production *via* the membrane process, an STC. This plant is operated in a stationary state at a  $Cl_2$  production rate of  $1 t_{Cl_2}/h$ . To enable a variable production, the plant has to be oversized. To enable a switchable operation, the current electrodes have to be replaced by bifunctional electrodes. Data from literature allows the estimation of the investment costs: according to Arnold et al.,<sup>33</sup> the estimation of the investment costs for expanding the capacity of a chlor-alkali electrolysis plant is not trivial and depends highly on the individual settings of the preexisting site. Therefore, only a broad range for the investment costs of €200 up to €1200 per yearly production of 1 ton  $Cl_2$  can be given in that publication. In the herein considered study, an oversizing of 10% of a plant with an initial  $Cl_2$  production capacity of 1 ton per hour is assumed. The additional capacity of 840 year-tons of  $Cl_2$  therefore leads to investment costs in the range of €168,000–€1,008,000 for a variable operation.

The investment costs for the conversion of a membrane cell with either an STC or an ODC to a switchable plant depends mainly on the new installation of bifunctional electrodes. For the conversion of a plant with production capacity of 1 ton  $Cl_2$  per hour, investment costs of about €900,000 are assumed.<sup>34</sup> In

**Table 2. Time of Return on Investment for Modification of a Chlor-Alkali Electrolysis Plant With Stationary Operation of an STC at  $1 t_{Cl_2}/h$**

	Savings per week (€/w)		Assumed investment costs (€)	Time of return on investment (years)
<i>Profile 1</i>				
STC-variable	358	Best case	168,000	9.0
		Worst case	1,008,000	54.1
<i>Profile 2</i>				
STC-variable	820	Best case	168,000	3.9
		Worst case	1,008,000	23.6
<i>Future profile</i>				
STC-variable	1442	Best case	168,000	2.2
		Worst case	1,008,000	13.4
Variable + switchable	2920	Best case	1,068,000	7.0
		Worst case	1,908,000	12.6



**Figure 11. Electricity cost savings and total operating cost savings for an increased cleaning duration.**

[Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

addition to the exchange of electrodes, also a 10% oversizing of the initial plant is needed to allow the variable production rate. In total, an investment in the range of €1.07–€1.9 Mio is needed, depending on the preexisting plant settings for a plant that is variable and switchable.

Assuming that the savings identified in the optimization are obtained every week, the amortization of the investment costs can be deduced. Considering the electricity price profile 1, representative for 2016, the calculated savings of variable operation of the currently installed STC imply an amortization of the investment costs after 9 years (Table 2), assuming low investment costs of €200 per yearly production of 1 ton  $\text{Cl}_2$ , or even 54.1 years if the necessary investment for oversizing the plant is at the upper bound of the given range (at €1200). The electricity price profile 2 that exhibits higher price fluctuations yields 3.9 or even up to 23.6 years until the return on investment of the necessary oversizing is achieved, depending on the necessary investment costs.

For the future price profile, a variable operation with an STC leads to an amortization of the investment costs after 2.2–13.4 years. If the initial plant is fitted with the bifunctional electrode and oversized to allow a switchable and variable operation, the return on investment can be reached after 7.0–12.6 years with the future electricity price profile. The conversion to operation solely with an ODC is not considered here, as it necessitates a conversion of the existing plant like for the installation of a bifunctional electrode, but the bifunctional electrode provides higher savings in operating costs.

### Influence of cleaning times

In this section, the influence of the cleaning time is analyzed. A change in the necessary cleaning duration is of interest, as, so far, there exists no estimate about the necessary time to remove  $\text{H}_2$  and  $\text{O}_2$  from the electrochemical cell. It has been previously assumed that cleaning takes 10 min. In this section, longer cleaning intervals are examined. Here, it is assumed that it takes 60 min to remove  $\text{H}_2$  from the chlor-alkali cell. Cleaning after the OD-mode may be faster as  $\text{O}_2$  is consumed by the reaction and it therefore has left the electrolyte faster after turning off the feed. Here, 30 min are assumed. This increase in cleaning duration increases the operational costs for the underlying future price profile by only 0.35%, despite the simultaneous effect of more necessary downtimes of the plant for cleaning (see the bar chart in Figure 11). Lower electricity costs of the latter scenario are achieved due to longer operation in the OD-mode.

### Conclusion

Herein the conducted analyses of optimal plant operation of a chlor-alkali process show that for the current prices ( $\text{H}_2$ ,  $\text{O}_2$ ,

and electricity price profile of 2016), operation with an STC is more economic than operation with an ODC. An oversizing of the plant for a variable operation with an STC looks promising for the real price profiles of 2016. If the oversizing can be implemented by low investment costs of €200 per yearly production of 1 ton  $\text{Cl}_2$ , the return on investment is reached after 3.9–9 years. Although, if higher investment costs are necessary for capacity extension, the amortization times may become too long for rentability.

For projected increases in renewable energy sources in the energy market, and corresponding increases in the electricity price and its variability, the variable operation of the currently installed STC should provide an economic advantage.

The installation of a bifunctional electrode allowing switching between the ST- and the OD-mode promises even higher savings in operating costs under such circumstances. The bifunctional electrode then can reduce the electricity costs by ~29% compared to the currently installed stationary operation with an STC. With the considered future electricity price profile, the investment can be amortized after 7.0–12.6 years.

In addition, longer cleaning intervals only have a small negative influence on operating costs. Hence, even though the necessary cleaning times are still under experimental investigation, the employment of bifunctional electrodes looks promising even for long cleaning intervals of up to 30 min for cleanODST and up to 60 min for cleanSTOD.

Further analyses need to consider that variable production rates may increase the wear of the process components and might have a negative impact on product qualities. In particular, the effects of load changes on the electrodes and the membrane have to be checked in future research projects. Both influences may affect the technical and economical meaningfulness of a variable and switchable  $\text{Cl}_2$  production. These analyses may also allow an alternative formulation to the above presented time-constraint on minimal duration of the reactive modes presented in “Modeling of transitional mode operation” section. An alternative formulation such as an economic penalty for mode switching can integrate the decision on minimal mode duration into the optimization *via* capturing the trade-off between faster switching and faster material degradation. Faster switching can increase the benefit during highly fluctuating market conditions. Faster material degradation leads to increased necessary replacement of parts and thus higher maintenance costs. This alternative formulation necessitates a good economic representation of such a penalty for mode switching and should be developed in future work when more information on material degradation due to mode switching is gathered.

Furthermore, as electricity spot prices are available only a limited time in advance, the required price forecasts for the scheduling horizon are always subject to uncertainty. This necessitates optimal scheduling decisions under uncertainty

and/or rescheduling over a moving horizon. For instance, Pattison et al.<sup>35</sup> introduce a moving horizon closed-loop scheduling approach and demonstrate the theoretical developments on the model of an industrial-scale air separation unit. In addition to such a receding horizon formulation, the herein considered approach could benefit from a more detailed market model of the day-ahead market, as the price determination at the German EPEX electricity exchange depends on bids of price and volume of demand and supply. Therefore, for future investigations, the incorporation of a receding horizon formulation with a market model of the electricity market and introduction of bidding variables into the optimization could be considered. Although, in the herein conducted study, the exact electricity price knowledge over the complete time horizon of 1 week is assumed to obtain a first economic estimation of the benefit of combined DSM with mode switching in chlor-alkali electrolysis.

In addition, a constant  $\text{Cl}_2$  provision for downstream processes presumes a constant operation of these downstream processes, although, this might not be the case. It might be beneficial to realize a time-dependent operation of these processes as well. However, the focus of the herein presented work lies solely on the operation of the  $\text{Cl}_2$  production, so that the necessary  $\text{Cl}_2$  provision is assumed constant. A variable  $\text{Cl}_2$  demand could be taken into account in future work.

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## Notation

$C = \{\text{Cl}_2, \text{H}_2, \text{O}_2, \text{NaCl}, \text{NaOH}, \text{H}_2\text{O}\}$  (index  $c$ ) the set of components  
 $E = \{1, 2\}$  (index  $e$ ) the set of linearization intervals of the linearized electricity demand  
 $M = \{\text{ST}, \text{OD}, \text{cleanSTOD}, \text{cleanODST}\}$  (index  $m$ ) the set of modes  
 $T = \{1, 2, \dots, t_n\}$  (index  $t$ ) the set of all time steps

## Binary variables

$y_{m,t}$  = determines whether mode  $m$  is active at time  $t$   
 $z_{mm',t}$  = indicates whether there is a transition from mode  $m'$  to mode  $m$  from time  $(t-1)$  to  $t$   
 $k_{m,e,t}$  = indicates whether a linearization interval  $e$  of the electricity demand of a mode  $m$  is active at time  $t$

## Continuous variables

$C_{C,t}$  = costs for each component  $C$  at time  $t$ , €  
 $C_{\text{El},t}$  = costs for electricity at time  $t$ , €  
 $\text{Expenses}_{m,t}$  = operating costs of mode  $m$  at time  $t$ , €  
 $\dot{m}_{C,t}$  = production rate of component  $C$  at time  $t$ , kg/s  
 $\dot{m}_{C,m,t}$  = production rate of component  $C$  in mode  $m$  at time  $t$ , kg/s  
 $\dot{m}_{\text{Cl}_2,\text{lin},m,e,t}$  =  $\text{Cl}_2$  production rate of mode  $m$  for linearization power demand in interval  $e$  at time  $t$ , kg/s  
 $m_{\text{SCl}_2,t}$  =  $\text{Cl}_2$  storage mass content, kg  
 $S_{\text{Cl}_2,t}$  = backup time of the  $\text{Cl}_2$  storage, s  
 $P_t$  = electrical power demand of the plant at time  $t$ , kW  
 $P_{m,t}$  = electrical power demand of mode  $m$  at time  $t$  if This mode was active, kW  
 $W_{\text{El}}$  = electrical power demand per production of 1 ton  $\text{Cl}_2$  at an operating point of 6 kA/m<sup>2</sup>, kWh/kg $\text{Cl}_2$

## Parameters

$a_{m,e}$  = gradient of linearized electricity demand of mode  $m$  in linearization interval  $e$ , kWh/kg  
 $b_{m,e}$  = y-axis interception of linearized electricity demand of mode  $m$  in linearization interval  $e$ , kW  
 $\dot{m}_{\text{Cl}_2}, \bar{m}_{\text{Cl}_2}$  = lower and upper bounds of the  $\text{Cl}_2$  production rate if a reactive mode is active, kg/s  
 $\dot{m}_{N,\text{Cl}_2}$  = constant downstream need of  $\text{Cl}_2$ , kg/s  
 $\dot{m}_{\text{Cl}_2,e}, \bar{m}_{\text{Cl}_2,e}$  = lower and upper bounds of the  $\text{Cl}_2$  production rates of each linearization interval  $e$ , kg/s  
 $\Delta \dot{m}_{\text{Cl}_2}$  = maximal allowable production increase/decrease per time step, kg/s<sup>2</sup>  
 $M_C$  = molar mass of each component  $C$ , g/mol  
 $p_C$  = specific prices for each component  $C$ , €/kg  
 $p_{\text{El},t}$  = specific costs for electricity at time  $t$ , €/kWh  
 $\underline{S}_{\text{Cl}_2}, \bar{S}_{\text{Cl}_2}$  = lower and upper bounds of the normalized storage content, s  
 $\Delta t$  = time step (length of time-discretization step), s  
 $\theta_{mm'}$  = minimal mode duration of mode  $m'$  after switching from mode  $m$  to  $m'$  given in number of time steps  
 $\theta_{\text{ramp}}$  = necessary time steps to ramp production from  $\bar{m}_{\text{Cl}_2}$  to  $\dot{m}_{\text{Cl}_2}$

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