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Assessing the realisable flexibility potential of electrochemical processes

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Abstract

Demand response is a viable concept to deal with and benefit from fluctuating electricity prices, and is of growing interest to the electrochemical industry. To assess the flexibility potential of such processes, a generic, interdisciplinary methodology is required. We propose such a methodology, in which the electrochemical fundamentals and the theoretical potential are determined first by analysing strengths, weaknesses, opportunities, and threats. Afterwards, experiments are conducted to determine selectivity and yield under varying loads and to assess the additional long-term costs

associated with flexible operation. An industrial-scale electrochemical process is assessed regarding its technical, economic, and practical potential. The required steps include a flowsheet analysis, the formulation and solution of a simplified model for operation scheduling under various business options, and a dynamic optimisation based on rigorous, dynamic process models. We apply the methodology to three electrochemical processes of different technology readiness levels – the syntheses of hydrogen peroxide, adiponitrile, and 1,2-dichloroethane via chloralkali electrolysis – to illustrate the individual steps of the proposed methodology.

Nomenclature

Abbreviations

ACN	Acrylonitrile
ADN	Adiponitrile
aFRR	Automatic frequency restoration reserve
AO	Anthraquinone oxidation
BCE	Biscyanoethyl ether
CAE	Chlor-alkali electrolysis
DCE	1,2-dichloroethane
DR	Demand response
DSM	Demand-side management
DynOpt	Dynamic optimisation
FCR	Frequency containment reserve
FS	Flowsheet
GDL	Gas diffusion layer
LCC	Costs of load change
LP	Linear programming (problem)
mFRR	Manual frequency restoration reserve
MILP	Mixed-integer linear programming (problem)
MINLP	Mixed-integer nonlinear programming (problem)
NLP	Nonlinear programming (problem)
OM	Operation model
ORR	Oxygen reduction reaction
PN	Propionitrile
SWOT	Strengths-Weaknesses-Opportunities-Threats
TCE	1,1,2-trichloroethane
TRI	1,3,6-tricyanohexane
TRL	Technology readiness level
TSO	Transmission system operator

Greek Symbols

Δ	Difference
ϕ	Weighting factor

Latin Symbols

A_{Geo}	Area of electrode, m^2
C	Costs, EUR or EUR a^{-1}
F	Faraday constant, $96\,485.3\,\mathrm{A\,s\,mol^{-1}}$

FE	Faraday efficiency, %
P	Load, power, W
Q	Total charge of system, C
S	Storage capacity, kg
S_P	Selectivity towards product, %
V	Volume, L
$\dot{V}$	Volume flow, $\mathrm{L\,h^{-1}}$
Y_P	Yield of product, %
W	Work, J
c	Molar concentration, $\mathrm{mol\,L^{-1}}$
f	Objective function
g	Process model
h	Path constraints
s	Signal
t	Time, s
t_gap	Time between two load changes, s
t_L	Latency time, s
t_P	Duration of load change, s
u	Manipulated variable (control)
Δu_max	Restriction for control change between control elements
$\dot{u}_\mathrm{max}$	Restriction for slope of control change
v_P	Rate of load change, $\mathrm{W\,s^{-1}}$
x	State variables
z	Number of transferred electrons

Indices

ce	Control element

Subscripts

0	Nominal operating point
addInv	Additional investment
BS	Balancing services
LCC	Costs of load change
down	Load decrease
el	Electrical
max	Maximum
min	Minimum
prod	Product
up	Load increase
var	Variable

1 Introduction

Flexible operation of chemical processes is increasingly demanded to tackle challenges, such as an increasing share of renewables in the electricity mix, feedstock restrictions, increasing costs, or quickly changing customer wishes [1]. However, chemical plants are usually optimised for a specific production capacity to minimise the sum of investment and operating costs [2]. Consequently, conventional plant operation is diametrically opposed to these new market developments. On the other hand, flexible operation also offers emerging opportunities [3], e.g. exploitation of varying electricity prices or financial compensation for providing grid balancing services. This is particularly true for electrochemical processes due to their high demand for electrical energy and a considerable share of electricity cost in the production costs [4]. If companies participate in these new markets, plants are either operated at high capacity in the case of low electricity prices and at low capacity in the opposite case [5–8] or load reduction / increase is offered to the transmission system operators (TSO) for stabilising the power grid [9]. Such operating modes are expected to become even more important in the future as the installed capacity of fluctuating renewables in the electricity mix and the electrification of transport and heating continue to increase whereas base-load power plants, such as coal-fired power plants, are being more and more decommissioned [10], thus creating the need for additional flexibility and storage capacity [11]. This form of load management is also known as demand response (DR) and poses a viable path for balancing the power grid or utilising price signals [12,13]. Many technologies and processes have been analysed in more depth concerning DR applications, including wastewater treatment [14], the chloralkali electrolysis [5,15–19], air separation units [20,21], and smart grids [22].

Compared to other possibilities, such as pumped-storage hydroelectricity, electrochemical processes are subject to more significant restrictions regarding their flexible operation as they are not primarily designed for balancing the power grid but for producing a nominal amount of chemicals. While the possible advantages of DR have been demonstrated, there is yet no generic, interdisciplinary methodology to quantify the potential, i.e. the actual available and realisable load change, of DR for electrochemical processes. Only Dranka and Ferreira [23] recently conducted a review in which they proposed a similar workflow for generic industry sectors, but their description of the necessary steps to be taken is rather short and contains few specifics. In particular, Dranka and Ferreira [23] do not give any details on how to quantify the potential and which specific steps are necessary to achieve this goal. Given the highly interdisciplinary aspects that must be considered for DR – such as process operation and control, economics, and material stability – a methodology that puts these aspects in a logical order and suggests criteria to evaluate them, is deemed highly beneficial. In other sectors, such methodologies have been suggested, e.g. the potential of buildings [24], heating systems [25,26], energy systems [27], or paper production plants [28].

Our methodology addresses both the required knowledge of electrochemical fundamentals as well as process-specific information, such as minimum and maximum load, the costs associated with DR, the various business options, and the regulatory constraints of DR. In addition, dynamic feasibility under varying load is ensured, i.e. relevant path constraints for product quality or allowable control changes are enforced. Note that this methodology is not meant to assess flexibility only from the standpoint of mathematical optimisation as suggested by Grossmann and Floudas [29] or Dimitriadis and Pistikopoulos [30]. Rather, it is intended to be a systematic guide to assessing whether a specific process could be made flexible and which bottlenecks might arise.

In the next section, we give a brief overview of demand response and possibilities for load management as well as the subcategories of flexibility potentials. Section 3 presents the proposed methodology to assess the realisable flexibility potential. Within this methodology, every potential type, i.e. theoretical, technical, economic, and practical potential, is assessed step-by-step. In Section 4, three case studies illustrate the methodology steps for three different electrochemical process of varying technology readiness levels: First of all, we focus on the synthesis of hydrogen peroxide in an acidic environment, which is still in an early development phase but which may be of high interest for flexible operation in the future.

Case study 1 presents results relevant for identifying appropriate process parameters in preparation for their implementation in a mini-plant. Secondly, we present results for the electrochemical synthesis of adiponitrile, which is well-established in the industry. However, the implications of its flexible operation for undivided electrolysis cells have yet not been studied. For this purpose, flexibility experiments are carried out to study the impact on yield and selectivity. Thirdly, we analyse the chloralkali electrolysis and the subsequent synthesis of 1,2-dichloroethane. This process is of considerable interest for DR and represents a real industrial application. The case study describes the necessary steps to assess the realisable potential, which include a detailed analysis of the flowsheet, the description of the costs associated with DR, the solution of an optimisation-based scheduling problem, and the solution of a dynamic optimisation problem to verify the feasibility of the operating schedule. Finally, the methodology is critically evaluated and future improvements are discussed.

2 Demand response and flexibility potentials

While some authors use the terms demand-side management (DSM) and demand response as synonyms, we follow the following broader definition for the former:

Definition 1 (Demand-side management[31]). *DSM is the planning, implementation, and monitoring of [...] utility activities designed to influence customer use of electricity in ways that will produce desired changes in the utility's load shape, i.e. changes in the time pattern and magnitude of a utility's load. [This includes] load management, new uses, strategic conservation, electrification, customer generation, and adjustments in market share.*

Demand response is a subcategory represented by the term 'load management'. Throughout this work, we will focus on load management when discussing DR potential:

Definition 2 (Demand Response[32]). *DR represents changes in the usual demand of electrical energy over time by the end-use customers in response to incentive payments or changes in the price of electricity.*

If a plant is subject to DR, loads can be reduced or increased. In the case of load reduction, the plant consumes less electricity than under nominal conditions. In times of load increase, the electricity consumption lies above its nominal value. However, load reduction will always imply a decrease in produced chemicals. This may be approached by either load shift or load relinquishment[22]:

Load shift: Customers reduce their normal (planned) production for a period of time and balance this shortfall later by load increase. Over time, these two cancel each other out and the nominal productivity is achieved[33]. A storage unit is a precondition to store the surplus in production. At times of low production, the planned production is maintained with the help of the storage tank.

Load relinquishment: In this case, the lost production is not compensated for later; therefore, the economic losses due to reduced productivity are expected to be more severe compared to load shift. Consequently, load relinquishment is only economic if the profit from flexibility is higher than the costs of product loss.

Distinguishing between these two options is highly important given that plants conventionally do not dispose of much additional capacity, and typically operate close to maximum capacity. For example, chloralkali electrolysis (CAE) has an average annual capacity utilisation greater than 95 %[34]. Load shift is therefore more onerous since the required overcapacity is usually lacking.

The presented load management strategies will ultimately lead to flexible operation with varying load for the plant / process in question, which is defined below:

Definition 3 (Flexibility[35])**.** *The flexibility of chemical processes includes both the number of options for operating conditions with feasible steady-state operating modes and the rate of switching between these operating modes, provided that safety, reliability, and quality requirements are ensured at any point in time.*

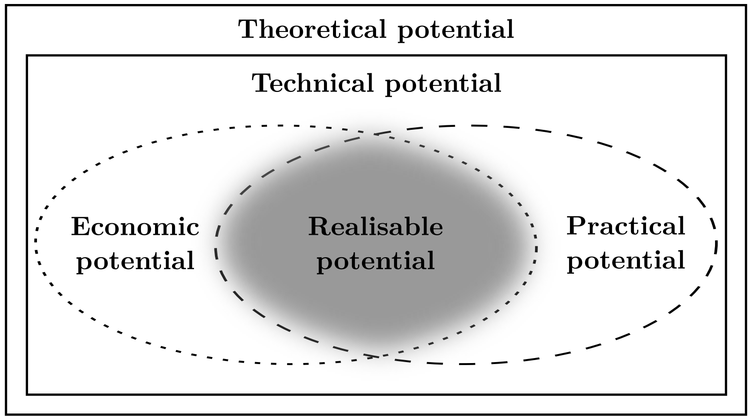

Figure 1: The different types of flexibility potentials and their relation for (electro-)chemical processes, based on Klaucke *et al.*[38] and Ausfelder *et al.*[34].

2.1 Types of flexibility potentials

It is evident from Definition 3 that flexibility of a process is influenced by reaction kinetics, process design, and process control. This definition of flexibility, however, is only an assessment of the technical feasibility under regulatory constraints. It is not considered whether these operating conditions are economically viable. Therefore, flexibility potential is only an umbrella term and can be further divided as has, for example, been done by Grein and Pehnt[36] or Gils[37]. However, there is yet no uniform classification. We adopt the definition given by Klaucke *et al.*[38] and extended by Ausfelder *et al.*[34], with five subcategories, namely theoretical, technical, economic, practical, and realisable potential (Figure 1).

The theoretical potential describes the maximum possible flexibility that is available for a chemical process. It is either computed from the installed capacity of a specific process (in case, we evaluate an established process with TRL ≥ 8) or from the capacity estimated to satisfy the market demand (in case, we evaluate a process still in development with TRL < 8). This theoretical potential is restricted by chemical and reaction engineering, process and control engineering, and infrastructure to yield the technical potential. Exemplary restrictions considered in the technical potential are the minimum allowable electricity consumption of an electrolyser cell, but also the required minimum load in a subsequent distillation column.

The economic potential is a subset of the technical potential. Flexible operation may lead to additional costs, e.g. product storage or enhanced plant maintenance. These costs need comparing to the economic benefit. Therefore, the economic potential includes all cost-effective and profitable implementations. The practical potential is another subset of the technical potential. Ausfelder *et al.*[34] defined this as additional intra-corporate, regulatory, and administrative constraints, e.g. ramp constraints for which the transient plant trajectories must remain feasible in specific demand response scenarios and markets. This way, not only the plant's capability to operate at reduced load is ensured but also its capability to achieve this operating mode safely, efficiently, and within these specific time constraints. The intersection of economic and practical potential yields the realisable potential. Only this potential could be realised economically by a company while adhering to constraints for product purity or control changes. However, most studies determine either the theoretical potential[37] or the technical potential[34] because much expertise and process knowledge is required to assess the limitations of a specific process.

2.2 Parameters determining the demand response potential

Load change scenarios are characterised by the following five parameters:

Minimum and maximum load: These parameters define the minimum allowed (P_{min}) and maximum allowed (P_{max}) load. No positive (ΔP_{up}) or negative (ΔP_{down}) load change may violate these bounds.

Rate of load change: The load change from one operating point to the other is usually realised as a ramp and does not occur instantaneously. The rate of a load change $\mathrm{d}P$ per time period $\mathrm{d}t$ is given by v_{P}.

Duration of load change: The time during which a load change occurs is given by t_{P}. This includes the two ramps and the time during which the process is operated at constant (reduced or increased) load.

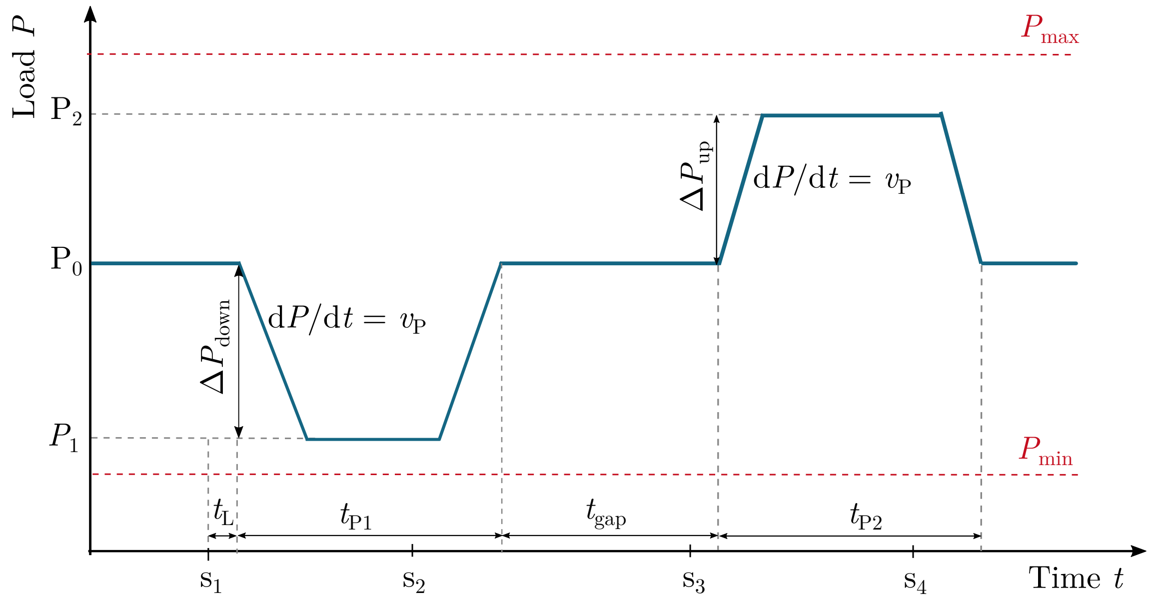

Figure 2: Schematic load profile to illustrate the parameters for assessing the practical potential of DR. Linear load changes are depicted for simplification and do not necessarily represent reality. ΔP: load change; v_P: rate of load change; t_P: duration of load change; t_{gap}: time gap between two load changes; t_L: latency between signal s for load change and measurable load change in the process; P_0: nominal load; P_1, P_2: reduced and increased loads due to DR, P_{min}, P_{max}: smallest and largest possible load.

Time gap between two load changes: This parameter t_{gap} defines the time that lies between two load changes.

Latency: This parameter t_L describes the delay between the signal s to initialise the load change and the effective, measurable load change within the process.

Figure 2 illustrates the meaning of these parameters in a schematic load profile. The parameters can either be given by process constraints, e.g. the minimum load, or they are determined by a particular business option, e.g. the rate of load change, as discussed in Section 3.4.2. Note that these parameters are, in general, no fixed values due to the nonlinearity of the studied processes. This will be further addressed in Section 3.3.2. Section 3 will outline how these different parameters can be assigned or determined.

Table 1: Description of TRL applied in chemical industry, adopted from Buchner *et al.*[40] and shortened for this work. See original work for extended version.

TRL	Title	Tasks
1	Idea	Identification of opportunities
2	Concept formulation	Technology concept / application, patent research conducted
3	Proof of concept	Experimental research in laboratory, qualitative observation of predicted reaction
4	Preliminary process development	Experimental concept validation, scale-up experiments, conceptual process design
5	Detail process development	Formulation of shortcut model
6	Pilot trials	Construction of mini / pilot plant
7	Final engineering	Performance optimisation for pilot plant
8	Commissioning	Integration of products and processes into organisation structure, construction of full-scale plant
9	Production	Audit of full-scale plant

3 Methodology

The proposed methodology to assess the realisable flexibility potential of an electrochemical process is presented in Figure 3. First of all, we differentiate between the electrochemical fundamentals as well as theoretical potential (left branch) and the industrial application (right branch). The technology readiness level (TRL) describes the maturity of a technology. There are nine levels, one being the lowest and nine the highest[39]. Although originally introduced for space travel technology, TRL has also been applied in the chemical industry, e.g. by Buchner *et al.*[40]. Table 1 contains a short description of every TRL to provide a better understanding of the proposed methodology. In the following sections, both branches and the steps within these branches are discussed in more detail. We begin with the left branch.

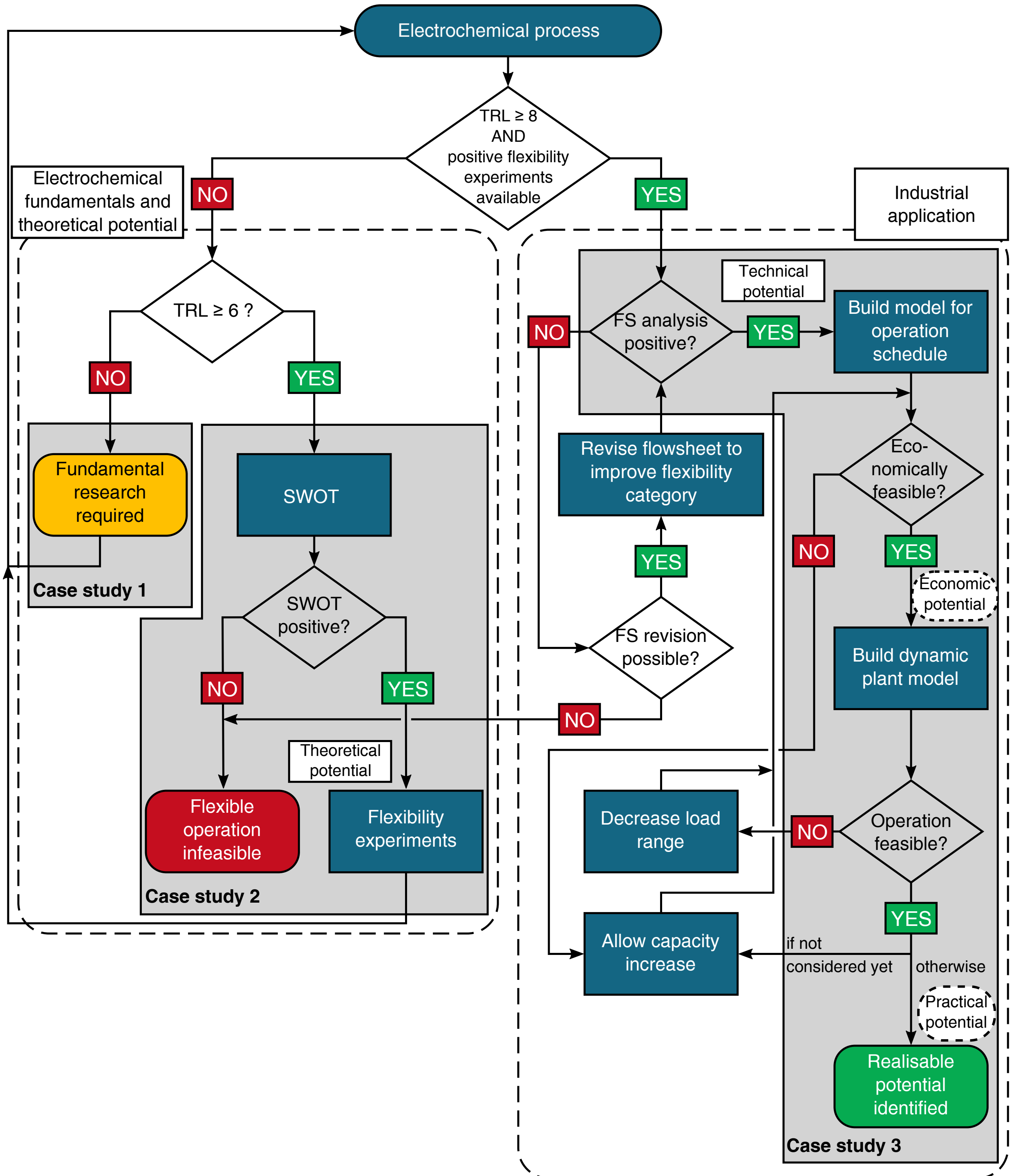

Figure 3: Proposed methodology to assess the realisable flexibility potential of an electrochemical process. TRL: Technology readiness level; SWOT: Strengths-Weaknesses-Opportunities-Threats; FS: flowsheet. The blocks mark which methodology steps are covered in each of the three case studies.

3.1 Electrochemical fundamentals and theoretical potential

Processes in the left branch with a TRL less than 6 have not been demonstrated in a mini-plant or pilot plant and there is hence not enough process knowledge to consider flexibility on an experimental scale. Should a considered process meet this criterion, more fundamental research is required. In this context, fundamental research refers to identifying new electrochemical processes that might replace conventional processes in the future and ultimately increasing the TRL of these processes so that flexible operation can be considered. Such a case is presented in case study 1 of this contribution.

For a process with a TRL larger than 6 but no available flexibility experiments, a qualitative analysis in a SWOT framework regarding different criteria adapted to the context is carried out to assess whether flexible operation would be, in principle, advantageous and if there are significant process-related or economics-related advantages compared to other process alternatives. In general, a SWOT analysis is an important tool derived from economics in which an internal analysis (strengths and weaknesses) is combined with an external analysis (opportunities and threats).[41–43] If process alternatives are compared, all information gathered from literature and experts needs to be sorted into these four categories to determine whether the currently investigated electrochemical process might be advantageous compared to other alternatives. Structuring the gathered information in a SWOT matrix helps in positioning oneself on the market and developing a strategy or recommendation. In this particular context, we use the framework of a SWOT matrix to decide whether flexibility experiments are feasible or not given possible competitors and process alternatives.

The investigated criteria for this attempt are:

- Product market size and product market development
- EHS (Environment, health and safety)
- Price and price development
- Price volatility (for oil, gas, and electricity)

- Security of supply

- Carbon footprint

If the strengths and opportunities of the process outweigh the weaknesses and threats regarding these criteria, we assume the analysis to be positive or successful and conclude that flexibility experiments should be carried out. While we only look at the number of positive entries in each category, one could also weight each category or even define exclusion criteria, i.e. criteria that immediately prohibit flexible operation. These may, however, vary from company to company and will depend on their strategy and their risk aversion. Hence, this qualitative analysis can be seen as a first proposal to make the ultimate decision.

3.2 Reaction parameters and flexibility experiments

Electrochemical processes may have complex reaction networks of both electrochemical and non-electrochemical reactions. Within these networks, many reactions are possible but not equally likely. Therefore, the reaction rates or equilibria will yield different amounts of products and byproducts, which ultimately determines the selectivity of the electrosynthesis.

Should the SWOT framework provide promising results, one may proceed with flexibility experiments to study the dependence of the electrochemical reactions on fluctuating parameters, e.g. current density. Reaction parameters, which are relevant for flexible operation and should thus be studied in depth in experiments, are defined in the following.

The selectivity S_P indicates the ratio of converted reactant into the desired product under consideration of the stoichiometry:

$$S_\mathrm{P} = \frac{n_\mathrm{P} \cdot (-\nu_\mathrm{E})}{(n_\mathrm{E,0} - n_\mathrm{E}) \cdot \nu_\mathrm{P}} \tag{1}$$

where n_P is the amount of desired product, ν the corresponding stoichiometric coefficient, $n_\mathrm{E,0}$ the amount of reactant E before and n_E the amount of reactant E after the reaction. The yield Y_P indicates the ratio of the amount of product n_P and the amount of educt $n_\mathrm{E,0}$

under consideration of the stoichiometric coefficient ν:

$$Y_{\mathrm{P}} = \frac{n_{\mathrm{P}} \cdot (-\nu_{\mathrm{E}})}{n_{\mathrm{E},0} \cdot \nu_{\mathrm{P}}} \tag{2}$$

The production rate r is the amount of product over a certain time normalised by the area.

$$r = \frac{n}{A_{\mathrm{Geo}} \cdot t}, \tag{3}$$

where n is the mole number of the desired product, A_{Geo} the geometric area of the electrode and t is time.

Finally, the Faraday efficiency FE is defined as the ratio of the Faradaic charge used to generate a desired product and the total Faradaic charge that crosses the electrocatalytic interface during a time interval:

$$FE = \frac{z \cdot c \cdot V \cdot F}{Q}, \tag{4}$$

where z is the number of transferred electrons, c the concentration of the product, V the electrolyte volume, F the Faraday constant, and Q the total charge of the system. From these metrics and experiments over a sufficient time horizon, conclusions can also be drawn regarding activity and stability of electrodes, membranes, etc.

These parameters must be studied experimentally to determine their sensitivity with respect to continuous load changes in order to (1) determine whether flexible operation is feasible and (2) allow for a cost estimate based on long-term stability experiments. For this purpose, the reaction parameters are monitored for applied load changes and are then compared to the results obtained for constant load operations. In addition, suitable process and operating parameters can be determined and their tolerable limits for flexible operation can be extracted. An example of this step of the methodology is given in case study 2 of this study.

This procedure of evaluating the TRL and conducting flexibility experiments is repeated until the process reaches Level 8 and it is possible to move over to the right-hand branch in

Figure 3.

3.3 Industrial application and technical potential

Once the process has reached sufficient technological maturity (TRL ≥ 8), the theoretical DR potential is known, but often of limited interest for an industrial application as it is restricted by the specific operating window of the process. These restrictions of the theoretical potential define the technical potential and should be evaluated based on a flowsheet (FS) analysis of a piping and instrumentation diagram (P&ID) of the process and other relevant data. The following paragraphs outline typical limitations of electrochemical plants that should be considered.

3.3.1 Process engineering

Electrochemical cell: State-of-the-art membranes for electrolysis are designed for low electrical resistance, high selectivity towards the preferred ion transport, and high chemical resistance against aggressive conditions in the electrolytes. To ensure these requirements, there is in general only a small operation window of the electrolyser regarding cell temperature and / or electrolyte compositions (i.e. pH value)[44]. Outside this operating window, increased damage to the membrane may occur due to impurities in the electrolytes (current density too low) and mechanical and thermal stress (current density too high). This window determines the applicable current density[45]. Modern electrodes also favour a specific operating temperature and / or composition ranges of the electrolytes as well as a desired range for the current density. Outside this window, ageing effects accelerate and damage to the electrodes increases[45].

Operating window of subsequent units: When a process is operated flexibly, the product flow will fluctuate over time. However, not every product can be stored easily and fluctuations are thus passed on to subsequent process units until an intermediate can be stored easily and safely. For example, storing chlorine produced via chloralkali electrolysis should be avoided whenever possible[15]. Up to this storage tank, all processes must also be operated flexibly. As plants are conventionally designed for specific operating conditions, deviating from them may not only result in decreased efficiency but also in an inoperable process, e.g. at the flooding point in a distillation tower. These absolute boundaries determine individual bounds on the load reduction ΔP for each process unit. This assessment of every single process unit will determine the flexibility bottleneck. Secondly, the number of downstream process units between electrolyser and storage tank is relevant: The more units are part of the flowsheet, the more units must operate flexibly. Their number is thus an indicator of how easily the process could be operated flexibly. Thirdly, highly heat-integrated or material-integrated plants pose a challenge for flexible operation.

Operating windows of peripherals: A significant share of a process consists of its peripheral elements, i.e. pumps, valves, measurement devices, pipes, etc. Of course, these also have minimum and maximum loads. Violating these may, for example, lead to increased wear, could further decrease the achievable operating points of process units, or induce gross error in measurements. Additional processing steps, such as drying, should also be evaluated with respect to their capacity.

Storability of chemicals: Additional storage is required to avoid load relinquishment and decreased sales revenue. In this context, a product's storability is of great importance for the flexibility potential of a process. If a product is not storable, load fluctuations will pass on to subsequent processes, which leads to a larger number of flexibly operating process units. When intermediate storage is integrated into a process, this intermediate product should

- have low environmental impact if released,
- not be highly toxic or highly reactive (preferably non-toxic and non-reactive),
- not noticeably decompose over a period of several days.

Additionally, the substances should be storable as liquids as these can be easily conveyed with smaller energy consumption and no phase change is required.

Feed availability: If the process is operated flexibly, feed streams to the electrochemical process and the subsequent process steps will also vary over time. However, feeds in chemical plants often stem from large facilities, e.g. crackers, with purchase quantities that were fixed in contracts. It is improbable that these large plants will be operated dynamically in the future. Instead, storage tanks might be necessary to ensure the availability of these feedstocks close to the plant. Consequently, it should also be checked whether all feedstocks can be stored safely.

3.3.2 Control engineering

Even if the process design allows for flexible operation, the actual dynamic operation also poses challenges for the control and plant automation. Conventionally, the control structure maintains the nominal operating point and set point changes are comparatively infrequent. In flexible operation, the number of transient phases increases and process stabilisation for a multiple-input-multiple-output system becomes more relevant. Hence, there are aspects that should be discussed from the view of control engineering.

Stability: One of the most important aspects is the stability of the process under considerable positive or negative load changes as they may lead to changing feed conditions for reactors or separation units. This, in turn, may cause hazardous runaway reactions, entry into an explosive atmosphere, or amplification of undesired side reactions or secondary reactions. As safety-related aspects should always supersede economic considerations, this aspect may drastically reduce the flexibility potential of a process as long as there are no suitable measures to mitigate their probability of occurrence or their effects on personnel or the environment.

Sensitivity: Changing feed amount and composition may also influences the amount and composition of product streams. It must be ensured that the process not only remains operable in DR-related load changes but also maintains product quality. Otherwise, economic losses due to off-spec production will quickly outweigh gains from marketed flexibility.

In our methodology, expert knowledge and standard sensitivity analyses are used to assess stability and sensitivity as they only require experience and a steady-state process model. However, stability could also be assessed by using fundamentals of control theory, see for example Albertos and Mareels[46], whereas sensitivity (or the possible range of input variables) could be determined in a flexibility analysis[29]. Case study 3 of this contribution will show that a our simplified approach generates reasonable limits for operation.

3.3.3 Categorisation

The relevant aspects for the FS analysis are summarised in Table 2. First of all, each aspect is assigned to a flexibility category A (high), B, C, or D (low)[47] based on the criteria in the second column. Column 3 of Table 2 provides possible properties to classify a criterion. Following the work of Klaucke *et al.*[47], the flexibility category of the whole process is set to the lowest of all subcategories. Note that the categorisation in column 3 of Table 2 is currently subjective as we only studied the chloralkali process in detail (see case study 3) and a broader analysis of electrochemical processes might suggest different ranges for the categorisation of the operating window, but it illustrates how such a categorisation can be performed.

We rank the storability of products or intermediates according to the criteria outlined above. Although a more quantitative analysis would be favourable compared to seemingly arbitrary keywords (low, moderate, ...), it is challenging to assign a numerical value to every criterion. Chemicals vary significantly in their properties, which must then be weighted against each other. In addition, safety regulations and requirements may vary from country to country. Hence, internationally valid chemical classifications[48] should be consulted and the storability of chemicals should be discussed with safety engineers in practise. Nevertheless, there are some tools that can be employed for a first analysis. This includes, for example, the NFPA 704 (typically used in the United States), which assigns a value between 0 and 4 to the categories health, flammability, and reactivity, but disregards other relevant properties, such as environmental impact. Moreover, such safety measures are typically published for pure components and defining a generically applicable method for mixtures (with additional properties) is thus challenging. In case study 3, we outline how this method could be applied, but we also show that this approach can be very misleading. There might be some potential in prediction methods as, for example, recently published by Linke *et al.*[49] that aim at evaluating all safety-relevant aspects simultaneously.

Using the outlined ranking approach has been shown to drastically decrease the flexibility potential of the chloralkali electrolysis, as only a few processes in the chlorine value chain can actually be operated flexibly[47]. This may help in focusing on the most relevant processes for flexible operation. The flowsheet analysis in Figure 3 thus specifies which processes actually offer technical potential for DR and should be further evaluated regarding their economic potential (category A). Category B (and potentially category C) may go through a re-design step in which the flowsheet is modified to remove the bottlenecks for flexible operation by adjusting process design or control scheme. If a flowsheet modification is impossible, flexible operation is deemed infeasible. This is always the case for processes in category D.

The bottom part of Table 2 contains the categorisation of the available minimum and maximum load of the process, P_{min} and P_{max}. This load range is divided into three categories. In category 1, for example, the load can be reduced by more than 20 % of the nominal load. On the other hand, the analysis will, in general, not yield information on v_{P}, t_{P}, and t_{gap} as these parameters are interdependent in practice. Instead, their values are determined by the specific requirements in the respective flexibility market as will be discussed in Section 3.4.

The final categorisation consists of the combination of the flexibility category and the load category, e.g. A3, which would indicate a process with excellent properties regarding

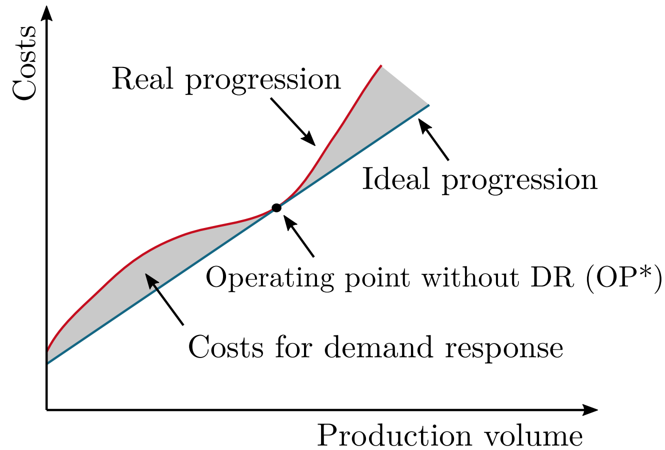

Figure 4: Definition of the costs of DR for load relinquishment.

process stability and product storability, but very limited load range. This numeral category may help when selecting appropriate business options in the assessment of the economic potential (next step in the methodology). For example, a process of category A3 would – as first approach – primarily operate in markets with small load range but high frequency.

3.4 Economic potential

Once the technical flexibility potential of a process has been successfully determined, the economic potential must be addressed (Figure 3). First of all, the costs of DR and its several business options are discussed. Secondly, these costs are related to the remaining DR parameters. Finally, a suitable model for operation scheduling is proposed.

3.4.1 Costs of demand response

Conventionally, continuous processes operate at the operating point OP*, which offers the lowest costs to achieve a certain capacity (Figure 4). In DR, the operating point deviates from OP*, which leads to increased costs. These costs deviate from ideal (linear) cost progression due to, for example, higher steam consumption, while losses due to load relinquishment are not considered at this point.

Figure 5 shows how DR costs can be further divided into provision costs and load change

Table 2: Flexibility categorisation and categorisation of load range based on flowsheet analysis, extended from Klaucke *et al.*[47].

Aspect	Criterion	Flexibility categorisation (A, B, C, D)
Process engineering		
Electrolyser	Damage to membrane or electrodes	None, mild, strong, severe
	Restrictions for heating/cooling	Yes or no
Subsequent units	Number of subsequent units	1, 2, 3, 4
	Boundaries for heating/cooling	Yes or no
	Degree of mass/heat integration	Low, moderate, high, severe
Peripherals	Valves, pumps, and compressors Heating/cooling Peripheral processing steps	Additional limitations? At which load?
Storability of product	State at ambient conditions	Solid/liquid or vapour?
	Environmental impact/toxicity	Low, moderate, high, severe
	Explosibility/flammability etc.	Low, moderate, high, severe
	Reactivity	Low, moderate, high, severe
	Decomposition	Low, moderate, high, severe
Feeds	Feed flexibly available	Yes or no
	Additional feed tanks required	Yes or no
	Storability of feedstocks	Refer to 'storability'
Control engineering		
Stability	Safety hazards (runaway, explosion range, ...)	Low, moderate, high, severe
Sensitivity	Impact on reaction temperatures	Low, moderate, high, severe
	Impact on separation efficiency	Low, moderate, high, severe
Operating window		
Assessed DR parameter(s)	Criterion for electrolyser and subsequent units	Categorisation of load range (1, 2, 3)
$P_{\min}$, $P_{\max}$	Maximum load reduction w.r.t. P_0	$> 20\,\%$; 5–20 %; $< 5\,\%$
	Maximum load increase w.r.t. P_0	$> 10\,\%$; 5–10 %; $< 5\,\%$

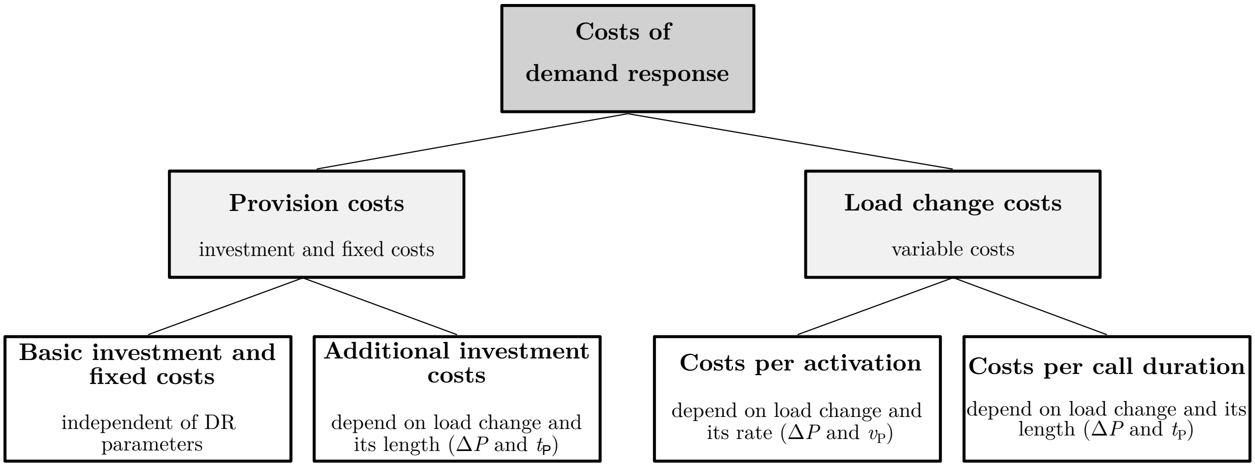

Figure 5: Classification of demand response costs and their dependence on the demand response factors.

costs (LCC). Provision costs concern the requirements for providing DR. They depend on the market demands, conditions of access (e.g. requirements for measuring technologies), production conditions, the required infrastructure on site (e.g. existing storage capacity or production overcapacity), and fixed costs (e.g. for personnel).

Provision costs consist of basic investment and fixed costs, which are independent of the DR parameters. The additional investments cost, e.g. for storage or overcapacity, depend on the positive and negative load changes, ΔP_{up} and ΔP_{down}, and their duration t_{P}. An example are the investment costs to create storage capacity.

Load change costs occur whenever the market requires a load modulation. They represent variable costs, particularly opportunity costs. These costs are divided into costs per activation and costs per call duration. The former depend on the amplitude ΔP and the rate of load change v_{P} (e.g. stress on equipment at beginning and end of rapid load changes) while the latter are influenced by the amplitude ΔP and the duration of the load change t_{P} (e.g. reduced product quality or even off-spec production).

These costs must be determined for all items that are most strongly influenced by load changes and the opportunity costs. This is essential for the calculation of the individual marginal price of DR. Concepts for estimating and determining the costs, particularly the provision costs, can, for example, be found in Peters *et al.*[50] and Sinnott and Towler[51]. In addition, many companies have their own databases for estimating equipment costs.

The costs per activation are more difficult to determine. At this point, long-term stability investigations as proposed in the left tree of our methodology become relevant: By comparing experimental results obtained for steady-state operation to results for flexible operation, the impact of fluctuating inputs can be quantified. In combination with known costs for renewing degraded process equipment, this allows for a good estimation of the costs per activation. Such an approach is illustrated by Hofmann *et al.*[19], who estimate the load change costs for the chloralkali electrolysis. Their approach will also be applied in case study 3. Other approaches have been proposed by Mitra *et al.*[52] or Obermeier *et al.*[53]. The challenge in their approach is to determine how many equipment starts are allowed within a certain time frame. Equally challenging is the determination of costs per call duration because effects, such as reduced quality, are often not considered in scheduling models. Therefore, we consider this an open research question and assume that product quality can always be maintained during operation as we can enforce that later on via dynamic optimisation with rigorous dynamic process models.

3.4.2 Business options

The business options depend on the power grid and its standards and structure. The grid is organised differently in every country and continuously changes to adapt to current challenges. Albadi and El-Saadany[54] classified existing DR programmes. They found that the option with minimum effort for DR-to-market is currently optimisation of the electricity purchase by using the available flexibility, which exploits temporary price spreads or price spreads in different markets. One example is the EPEX spot market, one of the most important electricity trade platforms in the EU where electricity is traded on two markets: the day-ahead market with hourly contracts for the next day and the intraday market where time slices of (at least) 15 min are traded until five minutes before the actual supply EPEX

SPOT SE[55].

Another business option is the participation in DR programmes of the transmission system operators (TSO), such as control reserve markets or capacity markets. These markets aim at stabilising the grid by balancing the fluctuations between supply and demand under consideration of the grid capacity[56]. Because of their systemic relevance, strict market regulations and access requirements apply. Söder *et al.*[57] summarised capacity markets for most European countries and the United States. Currently, an initiative supported by the European Network of Transmission System Operators for Electricity (ENTSO-E) standardises this market within the EU[58]. In the following, we consider the German balancing market, which is subdivided into the frequency containment reserve (FCR), automatic frequency restoration reserve (aFRR), and manual frequency restoration reserve (mFRR). Note that positive and negative aFRR and mFRR are traded independently.

The function, structure, and access requirements for these balancing markets are summarised in Table 3. The TSO initiates the load activation automatically (FCR and aFRR) or by communicating with the process operator (mFRR)[58]. An activation may occur at any time during the current time slice of four hours without the possibility of intervention by the process operator. Therefore, the time between two load changes t_{gap} may be zero.

3.4.3 Model for operation schedule

To determine the economic potential of DR, it is necessary to consider the monetary advantage of flexible plant operation compared to non-flexible operation that results from the utilisation of price spreads on the electricity markets or potential income from the provision of ancillary services. The level and volatility of market prices for the various flexibility options change over time as influencing factors such as regulation, market design and the nature of electricity generation and consumption change. For example, the increasing expansion of renewable energies and seasonal demands like heating or cooling lead to both increased diurnal and seasonal fluctuations in electricity prices.[61] To account for such long-term effects,

Table 3: Summary of the relevant parameters of the German reserve market.

	FCR	aFRR	mFRR
Function[58]			
	Rapid stabilization of grid frequency after disturbance event	Energetic compensation of the control zone and frequency control	Reserve to cope with longer lasting disturbances
Structure[58]			
Minimum bid	±1 MW	1 MW	1 MW
Time horizon	6 time slices with a length of 4 h each		
Payment	Pay-as-cleared load price	Pay-as-bid load price and price per MWh in the case of call	
Access requirements (pre-qualification)[59]			
Latency	$t_{\mathrm{L}} \leq 2\,\mathrm{s}$	$t_{\mathrm{L}} \leq 30\,\mathrm{s}$	$7.5\,\mathrm{min} \leq t_{\mathrm{L}}{}^{\mathrm{a}} \leq 22.5\,\mathrm{min}$[60]
Complete activation	Automatic, within 30 s	Automatic, within 5 min	Manual, within 15 min
Rate of load change	$v_{\mathrm{P}} \approx \Delta P/$ (activation time); quasi-linear ramp for load change		
Duration of load change	$t_{\mathrm{P,max}} = 15\,\mathrm{min}$	$t_{\mathrm{P,max}} = 20\,\mathrm{min}$	$t_{\mathrm{P,max}} = 20\,\mathrm{min}$

[a] Values for pre-qualifaction are not specified, typical values during operation are shown instead

the economic evaluation should be done for a sufficiently long time period and for different market scenarios, e.g. by comparing economic operation scheduling for different years based on historical data and forecasts.

The optimum operational trajectories for industrial plants are preferably determined using models for operation scheduling and based on mathematical optimisation. The operation scheduling model provides the optimum time profile of the power supply and the related production quantity depending on the input, e.g. fluctuating power price time series, and under consideration of one or more of the described business options. The relationship between the produced quantity and the purchased electrical power must be known.

Detailed process models of complete chemical plants are typically very complex and highly nonlinear. Their optimal solution over time horizons of several weeks, months, or even a year is challenging. Global optimal solutions of such nonlinear optimisation problems (NLP, MINLP) are frequently impossible to determine within reasonable time limits for such large time horizons[62]. Instead, the operation schedule can be obtained using a simplified model of the load curve as is the case for the model derived by us[19] and used in this contribution. Such a model is derived by solving a stationary model of the plant at varying load. If the system shows nonlinear behaviour, a simplification of the problem is possible, e.g. by using piecewise linearisation. The resulting (mixed-integer) linear optimisation problems (LP, MILP) can generally be solved much faster than the corresponding nonlinear problems. Another possibility to derive an operation scheduling model is the integration of simplified empirical process models as described in Pattison *et al.*[63].

The evaluation of the economic potential considers the variable operating costs, here mainly the electricity procurement costs and load change costs, plus the provision costs as shown in Figure 5:

$$\min_{P(t)} \quad C = C_{\mathrm{el}} + C_{\mathrm{LCC}} + C_{\mathrm{addInv}} \tag{5a}$$

$$\text{s.t.} \quad 0 = g\left(\dot{V}_{\mathrm{Prod}}, P, S, t\right) \qquad \text{(Simplified process model)}, \tag{5b}$$

$$P_{\min} \leq P(t) \leq P_{\max} \qquad \text{(Load constraints)}, \tag{5c}$$

$$0 \geq S(t) - S_{\max} \qquad \text{(Storage constraint)}, \tag{5d}$$

$$S(t_{\mathrm{start}}) = S(t_{\mathrm{end}+1}) \qquad \text{(optional: Load shift constraint)} \tag{5e}$$

This scheduling task is formulated as time-discrete, non-modal optimisation problem as has been done in prior research[64]. Other problem formulations can, for example, be found in Floudas and Lin[65] or Obermeier *et al.*[53].

In the stated optimisation problem, only $P_{\min}$ and $P_{\max}$ must be specified according to the boundaries identified in the flowsheet analysis. The same applies to the maximum storage level. The remaining DR parameters described in Figure 2 are neglected at this point, which leads to instantaneous load changes. In the case of load relinquishment, the costs of load change include opportunity costs due to reduced production, whereas load shift requires the consideration of an additional constraint to ensure that over- and underproduction are balanced over time.

The electricity procurement costs can be calculated based on historical price time series of wholesale electricity markets, such as the day-ahead market of the EPEX SPOT SE in the EU[55]. Another possibility is to use price forecasts for future years generated by electricity market models[66].

If additional markets, such as balancing services (BS), are considered, the resulting income is subtracted from the cost and additional constraints have to be introduced:

$$\min_{P(t)} \quad C = C_{\text{el}} + C_{\text{LCC}} - I_{\text{BS}} + C_{\text{addInv}} \tag{6a}$$

$$\text{s.t.} \quad 0 = g\left(\dot{V}_{\text{Prod}}, P, S, t\right) \qquad \text{(Process model)}, \tag{6b}$$

$$P_{\min} \leq P(t) \leq P_{\max} \qquad \text{(Load constraints)}, \tag{6c}$$

$$0 \geq S(t) - S_{\max} \qquad \text{(Storage constraint)}, \tag{6d}$$

$$0 \leq P_{\max} - P(t) - P_{\text{neg. BS}} \qquad \text{(neg. BS constraint)}, \tag{6e}$$

$$0 \leq P(t) - P_{\min} - P_{\text{pos. BS}} \qquad \text{(pos. BS constraint)}, \tag{6f}$$

$$P_{\text{min. BS}} \leq P_{\text{BS}} \leq P_{\text{max. BS}} \qquad \text{(min./max. BS offers)}, \tag{6g}$$

$$P_{\text{BS}}(t) = P_{\text{BS}}(t-1) \quad \forall\, t \in \Delta t_{\text{BS}} \qquad \text{(BS time slice spec.)} \tag{6h}$$

The difference between the current load and maximum / minimum load of the plant limits the volume of available balancing services. In Equation (6e) and (6f), the quantities $P_{\text{neg. BS}}$ and $P_{\text{pos. BS}}$ account for load increase and load reduction, respectively, if the process consumes electric power. Besides, the network operators specify minimum and maximum loads for balancing service offers. The provided balancing capacities must be identical during the time slices defined for the respective balancing service type.

The share of allocated load flexibility for each business option depends primarily on the interaction of the plant's technical characteristics and the individual risk tolerance of the operator as well as the economic attractiveness of the respective markets. Business options with high required load change rates v_{P} generally cause more significant challenges with large load changes ΔP (and thus large economic potential) than options with lower v_{P} and ΔP. A starting point to consider this may be the the load category identified in the flowsheet analysis. On this basis, options for participation in the various markets can then be examined for their economic and practical feasibility.

The comparison between the variable costs with and without the incorporation of such business options yields the monetary benefit of DR. Potential provision costs, such as investment costs, have to be included in further economic considerations such as payback calculations. On this basis, the concluding decision on the use of DR is made. However, this procedure is company-specific and also depends on other aspects, such as risk tolerance. When an economic potential has been successfully determined and has yielded a load trajectory, the practical (and thus the realisable) potential can finally be assessed (see Figure 3). If the obtained trajectories reveal little or no economic benefit, the plant design may also be changed by expanding plant or storage capacity (Figure 3).

3.5 Practical and realisable potential

To identify the practical potential, the obtained trajectories from the operation (scheduling) model are verified to be feasible under real operating conditions using validated dynamic process models. This includes the application of the actual DR parameters for load change and rate of load change depending on the activated business option at time t.

At this point, the question might arise why the economic analysis precedes the process dynamics. Here, we use the following reasoning: If one starts with dynamics, there is a wide range of load changes or load change rates that would have to be tested. It does not suffice to just perform one load change to demonstrate that the process is feasible for flexible operation

– load changes in balancing markets can occur repeatedly before the process can recover and return to the original operating point. Therefore, we start by obtaining an economically driven trajectory that shows a realistic profile for the considered cost structure. The only thing we need to check then is whether the process may follow the regulatory constraints, i.e. the time during which a load change must take place for a specific business option, given the constraints for control changes or other path constraints. This is a requirement to be able to participate in this market segment. In addition, studying economics first seems reasonable from the standpoint of practical application: Should a company look into flexible operation, we assume that the formulation of a linear scheduling model is a smaller barrier compared to a detailed, rigorous dynamic model, coupled with a dynamic optimisation. In case an economic potential is determined, the dynamic optimisation can be set up.

By using economically feasible trajectories, we ensure that only the overlap of both the economic and the practical potential is used to assess the realisable potential in Figure 1. The feasibility of these load profiles is shown by solving a dynamic optimisation problem:

$$\min_{u} \quad f(u, x) = \sum_i \phi_i f_i \tag{7a}$$

$$\text{s.t.} \quad 0 = g(u, x, \dot{x}, P, v_{\mathrm{P}}, t) \qquad \text{(Dynamic process model),} \tag{7b}$$

$$0 \leq h(u, x, P, v_{\mathrm{P}}, t) \qquad \text{(Path constraints),} \tag{7c}$$

$$u_{\mathrm{LB}} \leq u \leq u_{\mathrm{UB}} \qquad \text{(Absolute control bounds),} \tag{7d}$$

$$0 \geq \left| \frac{\mathrm{d}u}{\mathrm{d}t} \right| - \dot{u}_{\max} \qquad \text{(Ramp restrictions) or ,} \tag{7e}$$

$$0 \geq \|u_{ce-1} - u_{ce}\|_2 - \Delta u_{\max} \qquad \text{(Control change restrictions)} \tag{7f}$$

In this problem formulation, the objective f may, for example, be given as the deviations f_i between nominal set points (e.g. from the economic trajectories determined in the previous section) and the process values given by the solution of the rigorous dynamic process model. For example, these f_i could be represented by least-squares or absolute differences. If the variables that appear in the objective function are of varying order of magnitude, it is necessary to normalise these deviations with the nominal value of the respective variable. Other recent advances in the area of dynamic optimisation, such as nonlinear model-predictive control or the consideration of uncertainty can be found in Esche and Repke[67].

While the solution of this dynamic problem is no mathematical proof of the feasibility of the previously obtained trajectories, we still assume it to yield representative results provided that the dynamic problem is solved for a sufficiently large time horizon with multiple load increases and decreases. The dynamic optimisation problem is solved subject to the dynamic process model and potential path constraints due to variable bounds and control constraints, as well as ramp constraints imposed by the DR parameter v_{P}, which depends on the active business option.

There are several ways to consider control constraints: (1) limiting the maximum permissible control change from one control element ce to the next, given by $\Delta u_{\max}$ (piecewise constant control actions), or (2) limiting the maximum permissible ramp for control changes on one control element by $\dot{u}_{\max}$ (linear controls with continuity condition). Both $\Delta u_{\max}$ and $\dot{u}_{\max}$ must be set to realisable values and depend on plant specifics. A third option is to include controller equations in the process model and to define their set points as decision variables in the optimisation problem[68]. This approach has also been used in the context of demand response[21] and was recently extended to consider uncertainty in electricity prices[69]. The risk of this approach is a very aggressive control action on the occasion that the controller is not well tuned or controller saturation is not considered.

To increase confidence into the optimal solution and reveal potential improvements for plant operation, actual plant data should, where possible, be compared with results obtained from optimisation. Note that it is possible even at this stage that the dynamic plant model reveals an infeasibility. Depending on the cause of the problem during the dynamic optimisation, either the minimum or maximum load, $P_{\min}$ or $P_{\max}$, must be changed or the plant may not participate in a particular business option for DR. In such a case, the trajectories must be re-computed using the operation model from the previous step. This iterative procedure is repeated until (1) all trajectories are dynamically feasible and the practical potential has been determined or (2) the possible load range cannot be further decreased, e.g. because the economic advantage becomes too small. In this instance, the plant's capacity is allowed to be extended (see Figure 3) and another, larger iterative loop begins. Should the extension of the plant's capacity also reveal no considerable potential, the practical potential might be too small and flexible operation should be discarded, because the disadvantages outweigh the advantages.

Provided that feasible trajectories were indeed determined, i.e. economic trajectories exist, which do not violate maximum and minimum load of the process and are feasible under the regulatory constraints of the DR parameters, the realisable flexibility potential of an electrochemical process has successfully been assessed. This realisable potential represents the load that can actually be used for load management under economic criteria while also adhering to the plant-specific constraints on load changes. This procedure is illustrated in case study 3 of this study.

4 Case studies

Three case studies are presented to demonstrate the methodology's application. The methodology steps that are covered in each case study are marked in Figure 3. The case studies vary in their TRL so that different parts of the methodology can be presented in more detail. In particular, they shall emphasise the methodology's interdisciplinary approach towards research in DR:

1. Case study 1: Research on electrochemical processes may allow for the substitution of conventional non-electrochemical processes in the future, thus creating new flexibility markets.

2. Case study 2: Flexibility experiments on lab scale assist in identifying the impact of

flexible operation on selectivity and yield and will allow for a better estimate of the additional costs associated with flexible operation.

3. Case study 3: The combination of economically driven scheduling models and rigorous, dynamic process models ensures that the economic potential is reliably identified and that the obtained economic trajectories are in fact practical given the additional dynamic path constraints under dynamic operation.

4.1 Case study 1: synthesis of hydrogen peroxide

Case study 1 addresses the electrochemical synthesis of hydrogen peroxide (H_2O_2), which is conventionally produced using the homogeneously catalysed anthraquinone oxidation (AO) process[70]. The AO process consists of the hydrogenation of the anthraquinone derivate, followed by the reduction of oxygen.

Although the AO process is able to produce large amounts of H_2O_2 with an excellent selectivity, it requires high inputs of organic solvents and energy due to the subsequent extraction and distillation steps[71]. Hence, there are already several incentives to improve this process from the standpoint of sustainability and energy efficiency. In the context of demand response, additional benefits emerge as the AO process cannot directly offer load flexibility due to the lack of electrochemical reactions. Given the global industrial demand for H_2O_2 (4.5 Mt per year, expected demand increase of 3.5 % over the next seven years[72]) and its use in, for example, the pulp and paper bleaching industry[73], chemical synthesis[74], and wastewater treatment[75], the electrochemical H_2O_2 synthesis may thus serve as an illustrative example of replacing conventional with electrochemical processes that are then potentially able to participate in the flexibility market. Consequently, this case study shall not only address current research challenges in this area, but also raise the attention of electrochemists, process, and energy engineers to this aspect of process development.

In contrast to the AO process, the electrochemical production of H_2O_2 via the two-electron oxygen reduction reaction (2eORR) directly uses electricity in combination with the reactants water and oxygen. This reaction may take place under alkaline or acidic conditions (Equation (8) and (9)). A more detailed overview of the different reaction mechanisms can be found in Yeager [76].

$$\text{pH value} > 11.75: \qquad O_2 + 2\,e^- + H_2O \longrightarrow HO_2^- + OH^- \tag{8}$$

$$\text{pH value} < 11.75: \qquad O_2 + 2\,e^- + 2\,H^+ \longrightarrow H_2O_2 \tag{9}$$

The TRL of the electrochemical production of H_2O_2 via two-electron ORR also depends on the pH value of the electrolyte: An industrial process (TRL = 9) in an alkaline environment is readily available [40] (Dow-Huron Cells [77,78]), but the high alkalinity of the product limits its application because alkaline H_2O_2 solution are unstable [79,80]. We note that this instability already touches on the highly relevant aspect storability in the context of DR. This shows how fundamental research can facilitate the application of DR by investigating alternative reaction conditions at a very early stage of the process design phase.

Contrarily, process concepts under acidic conditions are currently under examination on a laboratory scale (TRL = 3–4 [40]). According to Figure 3, this requires more fundamental research to determine suitable reaction and process parameters (Figure 3) to elevate the TRL. Current research is mostly focused on the development of new ORR catalysts for the electrosynthesis of H_2O_2 [81], but the implementation of state-of-the-art research into mini-plants is also receiving increasing attention [82,83]. A prominent example of mini-plants are the so-called micro flow cells, which are able to mimic industrially relevant conditions, such as current density, electrolyte / gas flow rates, and active area. Consequently, they represent an important link between laboratory experiments and experiments in pilot plants. To address the described challenges, we study the application of commercial porous carbon gas diffusion layers (GDLs) in a micro flow cell as shown schematically in Figure 6. This implementation in a flow-through setup avoids transport limitations caused by the relatively low solubility of oxygen in aqueous electrolyte solutions. The applied GDLs consist of porous carbon layers

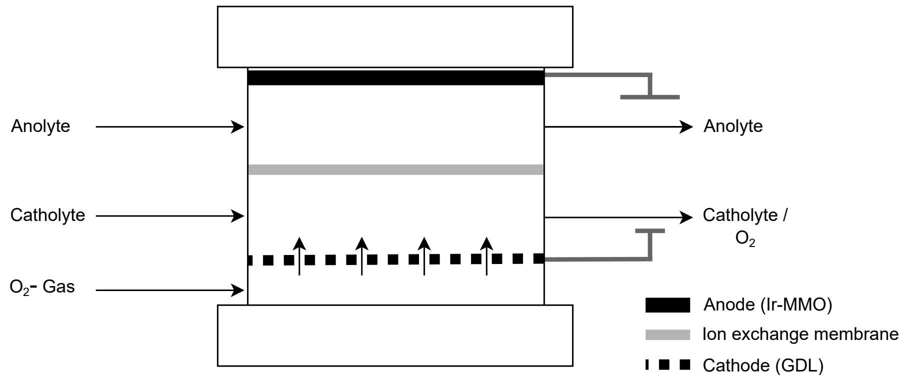

Figure 6: Schematic structure of the micro flow cell.

attached to carbon fibres. The experimental conditions realised in this micro flow cell are given in Table S1 in the Supporting Information.

Figure 7 shows the different production rates r and Faraday efficiencies FE for the H_2O_2 production using GDLs in different media within the flow cell. Their respective definitions are given in Section 3.1. Following Faraday's law, the production rates increase with the applied current density (Figure 7 (a)). The H_2O_2 production in 0.1 M H_2SO_4 (acidic media) shows the lowest Faraday efficiency and thus performs worse than 0.1 M KOH (alkaline media), see Figure 7 (b). The significantly lower Faraday efficiencies for the former result from the further reduction of H_2O_2 to H_2O at the GDL interface. This can be avoided by adding a small amount of K_2SO_4 to minimise the influence of this subsequent reaction. The results obtained with this mixture even exceed the FE under alkaline conditions. Figure 8 shows that the consumed electrical power P is lowest for 0.1 M H_2SO_4 + 0.05 M K_2SO_4 (acidic media), followed by 0.1 M KOH (alkaline media), and 0.1 M H_2SO_4 (acidic media). Since the electricity price is a relevant cost driver for electrochemical processes, the achieved performance improvements of the 2eORR indicate that electricity costs in alkaline and acidic media are comparable.

In spite of these promising improvements regarding the composition of the reaction me-

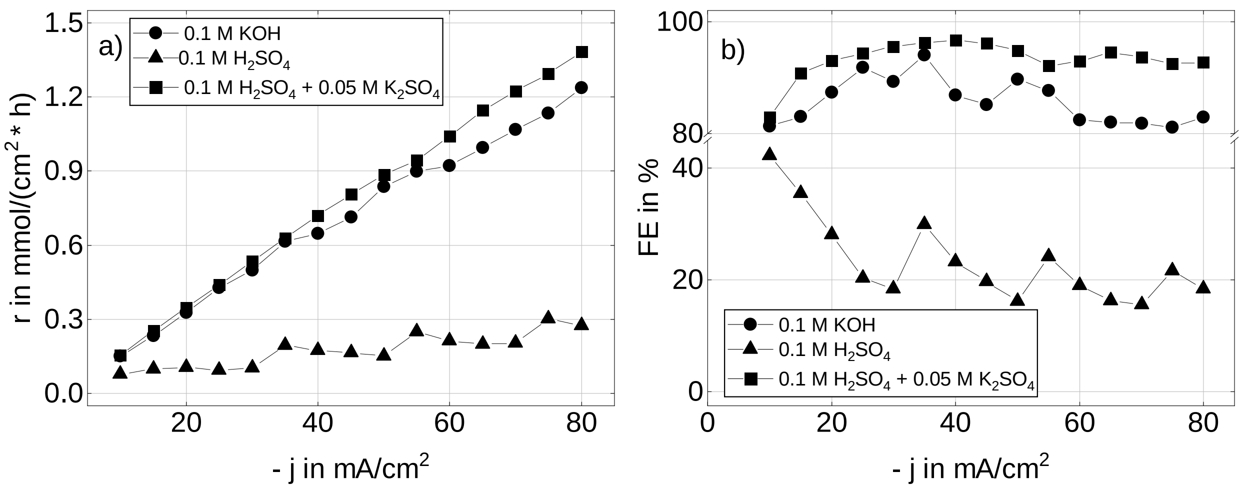

Figure 7: a) Production rates and b) Faraday efficiencies for 0.1 M H_2SO_4, 0.1 M KOH and 0.1 M H_2SO_4 + 0.05 M K_2SO_4.

dium, the next steps to complete TRL 4 will require a larger set of reproducible data points to demonstrate the proof-of-concept on laboratory scale and a first process concept that goes beyond the reaction itself, but also includes first ideas for the subsequent separation of H_2O_2. The advantage of processes in development is that flexibility considerations, which are often made retrospectively for processes on industrial scale, can directly be incorporated into this new process concept. Thus, process and energy engineers can contribute significantly even at this early design stage to ensure that the number of bottlenecks for flexible operation can be reduced whenever possible. This interdisciplinary approach will be beneficial for the flowsheet analysis in the right branch of Figure 3 as many potential issues were considered or even resolved early on.

4.2 Case study 2: synthesis of adiponitrile

The second case study addresses the 'Monsanto Process' for the production of adiponitrile from acrylonitrile (ACN). With a total production volume of 2.1 Mt in 2018, adiponitrile is considered a commodity chemical.[84] In 2014, the electrochemical synthesis route accounted for more than 300 kt of the total adiponitrile production, making it the world's largest industrially applied electro-organic process.[85,86]

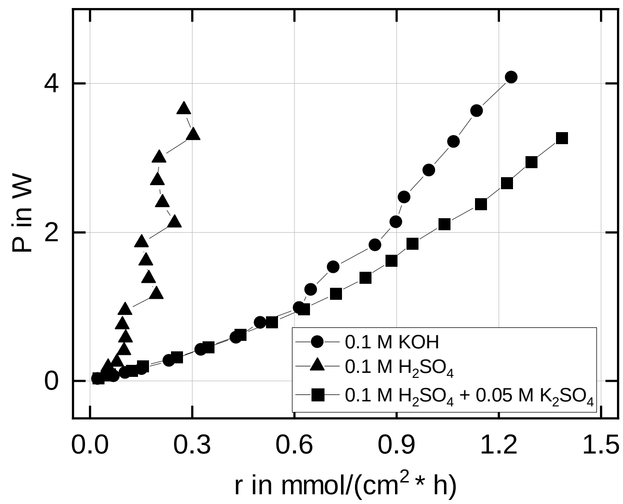

Figure 8: Power consumption P for 0.1 M H_2SO_4, 0.1 M KOH and 0.1 M H_2SO_4 + 0.05 M K_2SO_4.

Adiponitrile is an intermediate product that is further processed to Nylon-6.6 fibres and resins. In general, there are four different processes for the production of adiponitrile, which have already been applied on an industrial scale. The synthesis can be carried out via the dehydrating amination of adipic acid, the direct and indirect hydrocyanation of butadiene, and the electrochemical hydrodimerization of acrylonitrile.[87] Today, only the hydrocyanation and the hydrodimerization are relevant.[88] The majority of the world production of adiponitrile is made by the 'DuPont adiponitrile process'. This involves a double hydrocyanation of butadiene to ADN in the presence of a nickel catalyst. Based on the prognosis of increasing market demand, an electrochemical process alternative was developed by Monsanto in the early 1960s[89] and the Japanese company Asahi Kasei[90]. To increase the economic efficiency, both companies eventually developed a synthesis process with undivided cells[91] whose typical operating conditions are shown in Table S2 in the Supporting Information. The reaction takes places in a two-phase electrolyte, in which the organic phase consists of acrylonitrile and the by-products while the aqueous electrolyte contains a mixture of quaternary ammonium salts and phosphate salts.

The reaction mechanism of the electrochemical reaction of acrylonitrile to adiponitrile has not been conclusively determined. A widely held view is the formation of two anionic inter-

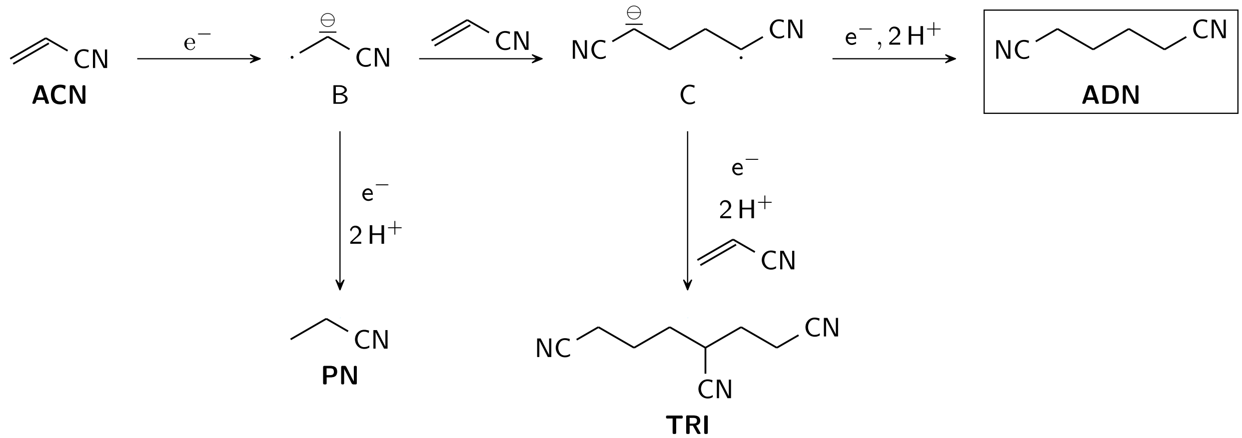

Figure 9: Reaction network of the cathodic electrohydrodimerisation from acrylonitrile.

mediates, the acrylonitrile radical anion (B) and the dimeric radical anion species (C) (Figure 9).[92–94] From B, both the by-product propionitrile (PN) and the second intermediate C are formed. The dimeric radical anion further reacts to form the trimer 1,3,6-tricyanohexane (TRI), and the main product, adiponitrile (ADN). Other byproducts are also possible, but propionitrile and the trimer are by far the most frequently observed.

4.2.1 SWOT analysis

While the TRL of the electrochemical process is clearly above 8 given its industrial application, no flexibility experiments have so far been reported. Blanco *et al.*[94] recently published first studies with pulsed voltage for a divided cell, but not for the usually applied undivided cell. Therefore, case study 2 also remains in the left branch of the methodology in Figure 3 and a SWOT analysis is carried out to estimate the theoretical potential for flexible operation. The results are shown in Table 4. Note that the results of this analysis do not have to be very detailed, but shall only help to determine whether the electrochemical process could be a promising DR option.

In summary, the advantages of the electrochemical synthesis of adiponitrile based on the Monsanto process outweigh the disadvantages as there are many aspects that favour this process concept, especially when renewable energy sources are used. However, the economics of this process and its competitiveness compared to alternative routes, especially when

Table 4: SWOT analysis for the Monsanto process.

Strengths	Weaknesses
• Aqueous electrolyte consisting of easily recoverable salts instead of a catalyst complex with ligands[95] • Only one synthesis step instead of three for the DuPont process[95] • Oil and gas prices have low impact on this process • Moderate operating conditions (atmospheric pressure, 55 °C)[86,94] • Undivided cell yields a robust configuration[89]	• Acrylonitrile and cadmium are harmful for health and environment • Oxygen and hydrogen are produced at anode and cathode, which is a potential safety risk[89] • Electricity price has a larger impact • Large carbon footprint when using electricity from fossil fuels • Significant capital investments[84]
Opportunities	**Threats**
• Continuously high demand for nylon-6,6, which is currently not substitutable[84] • Structural shortage of feedstocks, which are not substitutable • Market dominated by only a few competing suppliers • Carbon footprint can be reduced by using electricity from renewables	• Butadiene route still more economically favourable and competitors on the market are stronger

combined with DR, needs to be studied in more detail. Hence, the qualitative analysis in the SWOT framework is deemed positive and flexibility experiments for the electrochemical production of adiponitrile are carried out to determine the potential of the Monsanto process for this strategy.

4.2.2 Flexibility experiments

A setup based on the model of Scott and Hayati[96] was reproduced in the laboratory to investigate the feasibility limits of load changes in terms of selectivity and yield of the desired product (Figure 10). The reaction takes place in a parallel plate electrolysis cell (1) in which the voltage is kept constant with a potentiostat (11). The electrolyte temperatures

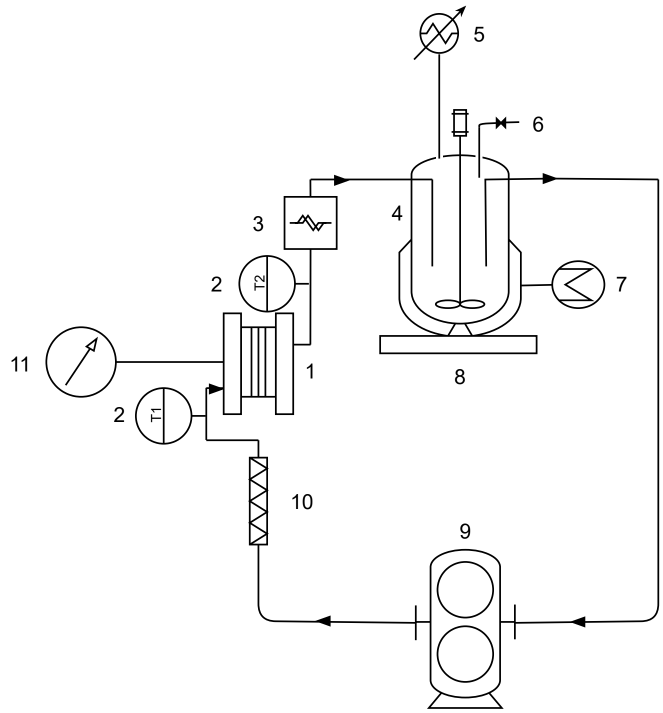

Figure 10: Setup for flexibility experiments for the electrochemical production of adiponitrile. 1: parallel plate electrolysis cell, 2: thermocouples, 3: Coriolis flow meter, 4: electrolyte storage with magnetic stirrer, 5: reflux condenser, 6: sample valve, 7: thermostat, 8: magnetic stirring plate, 9: gear pump, 10: static mixer, 11: potentiostat.

are measured with thermocouples before and after the cell (2) and the electrolyte flow is monitored using a Coriolis flow meter (3). The electrolyte is collected in a tank (4) where it is constantly stirred (8) to disperse the oil phase in the water phase. The tank's temperature is monitored using a thermostat (7). Possible acrylonitrile vapour is condensed using a reflux condenser (5) while non-condensable gases produced at the electrodes may leave the system through the vent. A gear pump (8) feeds the electrolyte through a static mixer (9) into the electrolysis cell.

Initial experiments were performed at constant current densities to establish a benchmark (Figure 11). Lower current densities imply lower conversion to adiponitrile with an increased formation of the trimer. More adiponitrile is formed with increasing current density. Above a certain level, the formation of the by-product propionitrile increases while the formation of the trimer decreases. This is also in agreement with observations in the literature.[96]

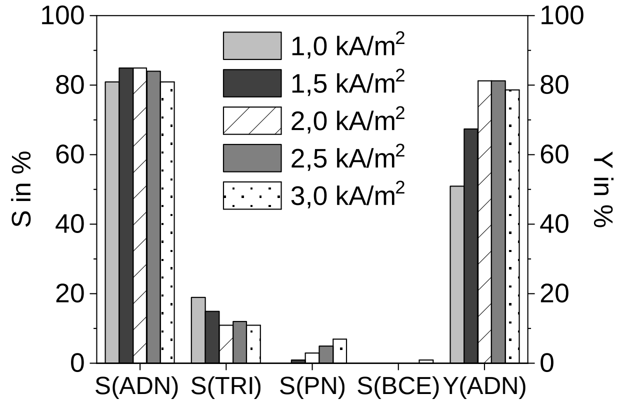

Figure 11: Selectivity towards adipontrile (ADN), the trimerization product (TRI), and propionitrile (PN) and yield of ADN at constant current density after six hours of reaction time.

Furthermore, bis-cyanoethyl ether (BCE) is observed at a current density of $3\,\mathrm{kA\,m^{-2}}$. The higher percentage of trimer at lower current densities can be explained by the mass transport limitation in the system, which promotes oligomerisation. The formation of propionitrile at higher current densities is the expression of a poorer current efficiency, since injected electrons are also consumed by other reaction paths in the reaction network (see Figure 9).

Afterwards, a series of load decreases and subsequent load increases of 25 % of the current density were performed over different time periods for a total of 360 minutes (Figure 12). The experimental data show that the selectivity towards adiponitrile as well as the activity hardly vary under this flexible operation. When increasing the current density after the reduction, the previously described effects cancel each other out, and no overall changes can be observed. Therefore, only load reductions were investigated in the following experiments. The effects of different load changes applied for 6 minute periods are compared in Figure 13. Again, no significant changes in selectivity of products can be observed. Although the yield of adiponitrile is slightly lower when 25 % and 50 % load changes are applied, due to the lower average current density, the yield is still higher than for a constant load profile with the same average current density ($1.5\,\mathrm{kA\,m^{-2}}$) as shown in Figure 14. Pulsation of the corresponding voltage could therefore lead to further improvements, similar to the observations in the literature for divided cells.[94]

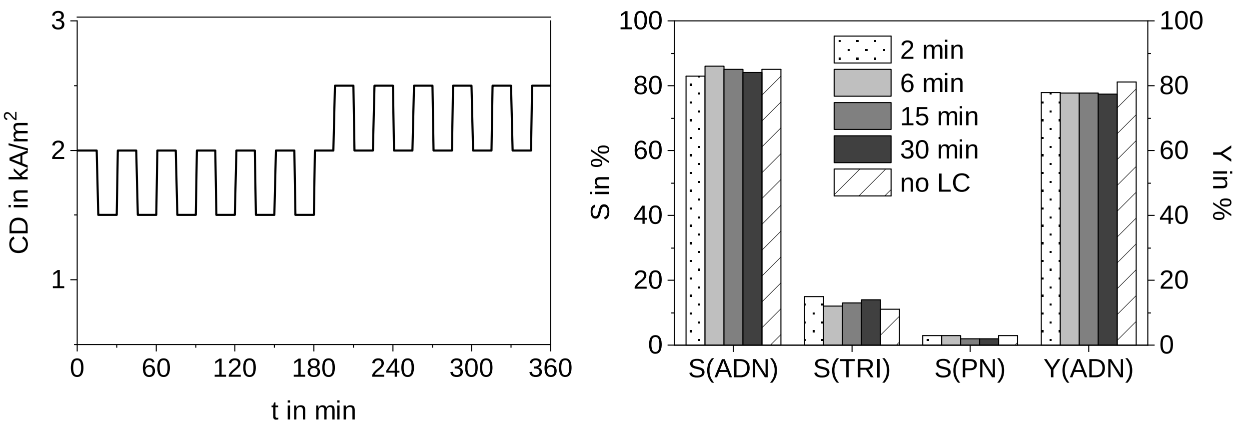

Figure 12: a) Example of an operation profile with load changes of 25 % for 15 minute periods. b) Selectivity towards adiponitrile (ADN), the trimerization product (TRI), and propionitrile (PN) and yield of ADN with a change of current density by $0.5\,\mathrm{kA\,m^{-2}}$ over varying time periods.

In summary, the present reaction setup for the electrohydrodimerization of acrylonitrile is sufficiently robust so that flexible operation does not cause any significant decreases of activity or selectivity in the electrolysis cell. In fact, an even higher yield could be observed than with a constantly applied current density. Consequently, the next step is to find the limits of this process by applying increasingly frequent and higher load changes. The consequences of a flexible operation on the stability must also be considered. To this end, the ageing of the electrodes after several load changes will be investigated in the future. Scanning electron microscopy measurements of the electrode surfaces are planned, supported by electrochemical impedance spectroscopy investigations. With this information, the operating window of the process can be identified and load change costs (LCC) can be estimated. Given the global production volume of 2.1 Mt, adiponitrile has a theoretical global potential for demand response of 582 MW, most of which is in China.

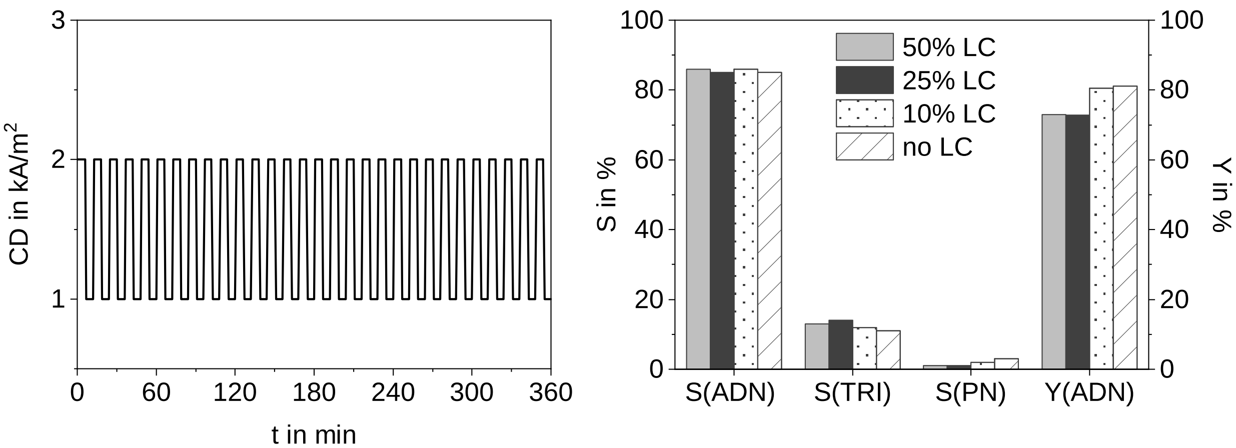

Figure 13: a) Example of an operation profile with a load decrease of 50 % for 6 minute periods. b) Selectivity towards adiponitrile (ADN), the trimerization product (TRI), and propionitrile (PN) and yield of ADN with varying load changes for 6 minute periods compared with a constantly applied current density of $2\,\mathrm{kA\,m^{-2}}$.

4.3 Case study 3: chloralkali electrolysis and synthesis of 1,2-dichloroethane

The third case study analyses the chloralkali electrolysis (CAE) in which hydrogen (H_2), chlorine (Cl_2), and sodium hydroxide (NaOH) are produced. The latter two are commodity chemicals and among the ten most-produced chemicals worldwide[97]. The CAE is an active research field, especially for DR applications. Studies have found a theoretical DR potential of more than 1 GW in Germany[34,38] for the CAE (not including downstream processes). However, chlorine production via CAE cannot operate flexibly as a stand alone process because Cl_2 storage is strictly limited due to safety concerns[15]. Klaucke *et al.*[47] reviewed different processes within the chlorine value chain and determined how the theoretical potential of the CAE is distributed among these. All investigated processes have a TRL of 9. However, there has been hardly any experimental research on the long-term impact of flexible operation on electrodes and membranes for CAE, as also pointed out by Roh *et al.*[98]. This is why we advocate for such a criterion in our methodology before evaluating the flexibility potentials. In the following, we assume that such research is available, given that the CAE is already operated flexibly in the industry to a certain extent, and therefore we move to the right

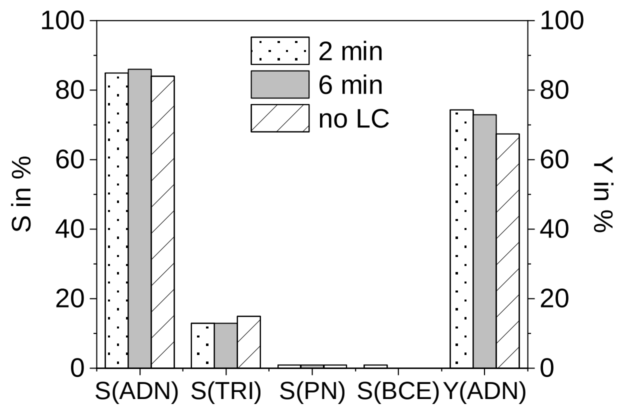

Figure 14: Selectivity towards adipontrile (ADN), the trimerization product (TRI), and propionitrile (PN) and yield of ADN for loadchanging profiles with an average current density of $1.5\,\mathrm{kA\,m^{-2}}$ compared to a constantly applied current density of $1.5\,\mathrm{kA\,m^{-2}}$ after 6 hours reaction time.

branch in Figure 3. Here, we will limit ourselves to CAE in combination with the production of 1,2-dichloroethane (DCE) and refer the reader to Klaucke *et al.*[47] for information on the other processes.

4.3.1 Technical potential of DCE synthesis

To study the technical potential of CAE and DCE production, consider the flowsheet of a combined CAE / DCE plant with a nominal power of 100 MW and an installed power of 105 MW (Figure 15), i.e. there is an overcapacity of 5 %. In the CAE cells, electric power is used to convert aqueous sodium chloride ($NaCl_{(aq)}$) to sodium hydroxide ($NaOH_{(aq)}$), chlorine (Cl_2), and hydrogen (H_2):

$$2\,NaCl + 2\,H_2O \longrightarrow 2\,NaOH + Cl_2 + H_2 \tag{10}$$

While NaOH is sold, the chlorine is dried, compressed, and fed into a reactor along with ethene (C_2H_4) to produce DCE:

$$Cl_2 + C_2H_4 \longrightarrow C_2H_4Cl_2 \tag{11}$$

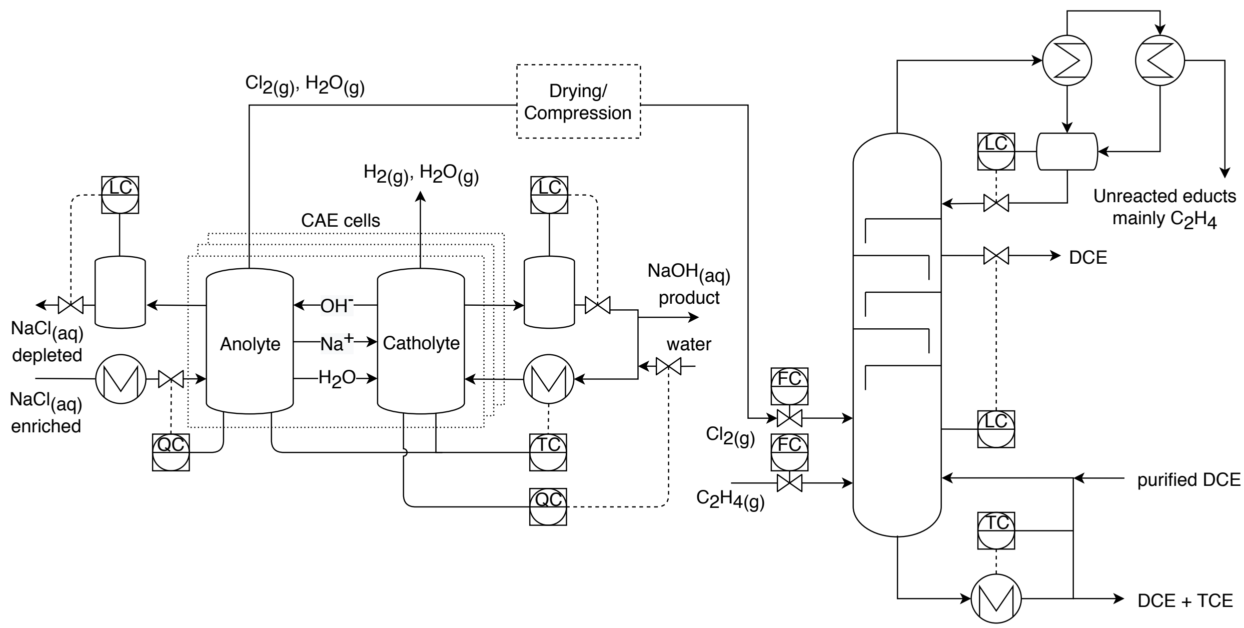

Figure 15: P&I diagram of CAE and DCE production.

This reactor serves simultaneously as reboiler for the distillation tower to purify the produced DCE. Note that other setups in which reaction and thermal separation of DCE are conducted in two different units are also possible, but are not the subject of this contribution. The DCE removed at the bottom is separated from the undesired by-product 1,1,2-trichloroethane (TCE) in a discontinuous external step and returned to the reactor[99,100]. Excess reagents leave the column at the top and may be recycled or used in secondary reactors. For the CAE, the depicted control loops may manipulate the feed of water, the outlet flows from the buffer tanks, and the feed temperatures of the cell. In the DCE production, the ethene feed, the reflux from the reflux drum, and the product flow represent manipulated variables. In addition, the heat removed in the heat exchanger at the bottom represents a degree of freedom. More details can be found in Weigert *et al.*[101] and Hoffmann *et al.*[100].

The results of the flowsheet analysis are presented in Table S3 in the Supporting Information. As part of this analysis was already carried out in Klaucke *et al.*[47], we only give a brief review here. The CAE in combination with DCE production has excellent properties with respect to flexible operation. These result from the sequential flowsheet with only one process unit after the CAE and the low sensitivity of the reaction to changing feeds. While DCE is certainly not completely safe, as it has some of the typical properties of organic chemicals, it may still be stored easily without much effort. This assessment is in agreement with another study on the flexibility potential of this process[34] and our own discussions with industrial partners. To assign a number to the storability of DCE, its fire diamond is discussed: DCE is assigned 2 (health), 3 (fire), and 0 (reactivity), averaging to a value of 1.67, which seems to be in good agreement with our own assessment. However, if we looked at chlorine (health: 4, fire: 0, reactivity: 0), this would average to 1.33, i.e. an even smaller value. Nevertheless, DCE storage is strongly preferred as a storage medium over chlorine in practise as outlined by Brée *et al.*[15] and confirmed in discussions with our industrial partners. Hence, using such simple measures can be misleading, even for pure components.

Moreover, additional periphery does not impose additional restrictions, and although long-term stability of membranes and electrodes is potentially an issue, there is no published data available that would confirm this concern. The process is therefore assigned to flexibility category A and we may proceed to the next flexibility level.

The load categorisation of the process is addressed at the bottom of Table S3. The CAE is limited by the appearance of chloride ions in the caustic soda at low loads ($3.6\,\mathrm{kA\,m^{-2}}$), which causes the product quality to leave the tolerable range. This value is even more restrictive than the $3\,\mathrm{kA\,m^{-2}}$ stated by Otashu and Baldea[17]. To determine this bound, measurements (from the industrial plant) of the chloride ion concentration in the catholyte were analysed. At high loads, the CAE is limited by a current density of $6\,\mathrm{kA\,m^{-2}}$, which is the maximum permissible current density of a typical CAE membrane. The DCE production is mainly restricted by minimum and maximum gas load in the distillation column. These restrictions were determined in discussions with industrial partners and could be confirmed independently in sensitivity studies by using our steady-state process model[100]. Based on these limitations, the process is assigned to load category 1 for load decrease and 2 for load increase. In summary, the CAE in combination with DCE production has a considerable technical flexibility potential and also covers a large load range, which allows for applications in various markets.

4.3.2 Economic potential of DCE synthesis

The initial examination of the possible savings due to flexible plant operation is conducted by setting up a model for operation scheduling as proposed in the methodology in Figure 3. Here, a steady-state process model of the combined CAE / DCE plant was set up. This model was used to determine the operating characteristics of the process and to obtain a load-dependent function of the DCE production. A complete description of the process and the operation scheduling model, as well as the discussion of the obtained results can be found in Hofmann *et al.*[19].

Following the results for the technical potential, we assumed a maximum load of $P_{\max} = 1.05P_0$ and a minimum load of $P_{\min} = 0.75P_0$. In this case study, we chose to only participate in the day-ahead market, which is described in Section 3.4.2, to illustrate our methodology. Scenarios with combined business options, such as balancing services, and their economic impact will be investigated in a separate, more focused study. As outlined, we initially assume that the plant has no further restrictions concerning the DR parameters, which must be validated later (Section 4.3.3). In the following, we always assume that load shift is applied to ensure the nominal production volume. Therefore, we set a value of $S_{\max} = 200\,\mathrm{t_{DCE}}$ for the storage capacity, which corresponds to $156.4\,\mathrm{m}^3$ or a stationary nominal operation of the subsequent cracker of 4 h.

Electricity procurement costs are calculated using the annual time series of day-ahead prices for 2018 and 2019 on EPEX SPOT[102]. To determine the LCC, knowledge of the influence of load changes on components such as the membranes is required. As this information was not available at that time, specific LCC of €5000 per full load cycle were derived based on theoretical considerations[19].

The results of the optimal operation scheduling are shown for both years in Table 5. The

Table 5: Optimisation results of the operation scheduling model developed in Hofmann *et al.*[19].

Year	2018		2019	
c_{LCC} in € /cycle	0	5000	0	5000
C_{el} without DR in € million	38.95		33.00	
C_{el} with DR in € million	37.63	37.77	31.83	31.99
Reduction of C_{el} with DR in € million	1.32	1.18	1.17	1.01
in %	3.39	3.03	3.54	3.06
C_{LCC} in € million	-	0.18	-	0.16

optimisation was also carried out with specific LCC of € 0 per cycle to analyse their impact on the load profile, i.e. load changes do not cause additional costs. We found that savings of more than € 1 million (more than 3 %) are possible for the annual electricity procurement costs in all cases. In contrast, the annual LCC in the corresponding cases amount to only 15–16 % of these savings. We refer to Hofmann *et al.*[19] for a more comprehensive discussion of the influence of the DR parameters and the LCC as part of a sensitivity analysis.

Figure 16 shows 1000 h of an optimal load trajectory for $c_{\mathrm{LCC}} =$ € 0 per cycle, denoted as LCC0, and $c_{\mathrm{LCC}} =$ € 5000 per cycle (LCC5) as a result of the operation scheduling. Here, the plant is operated at maximum load during times of low electricity prices. As a result, the storage level increases so that the load can be reduced to lower the electricity procurement costs when electricity prices are high. The storage then ensures the supply of the downstream process units. The operation trajectories show a significantly more flexible operation for neglected LCC (LCC0). This illustrates the importance of a precise determination of the load change costs, which is why early flexibility and stability investigations are part of our methodology.

As plant capacity and design were fixed in this first iteration, the provision costs are zero and no further investment calculations are required. Based on these results, we consider the economic implementation of DR to be feasible and advantageous. In reality, a company may

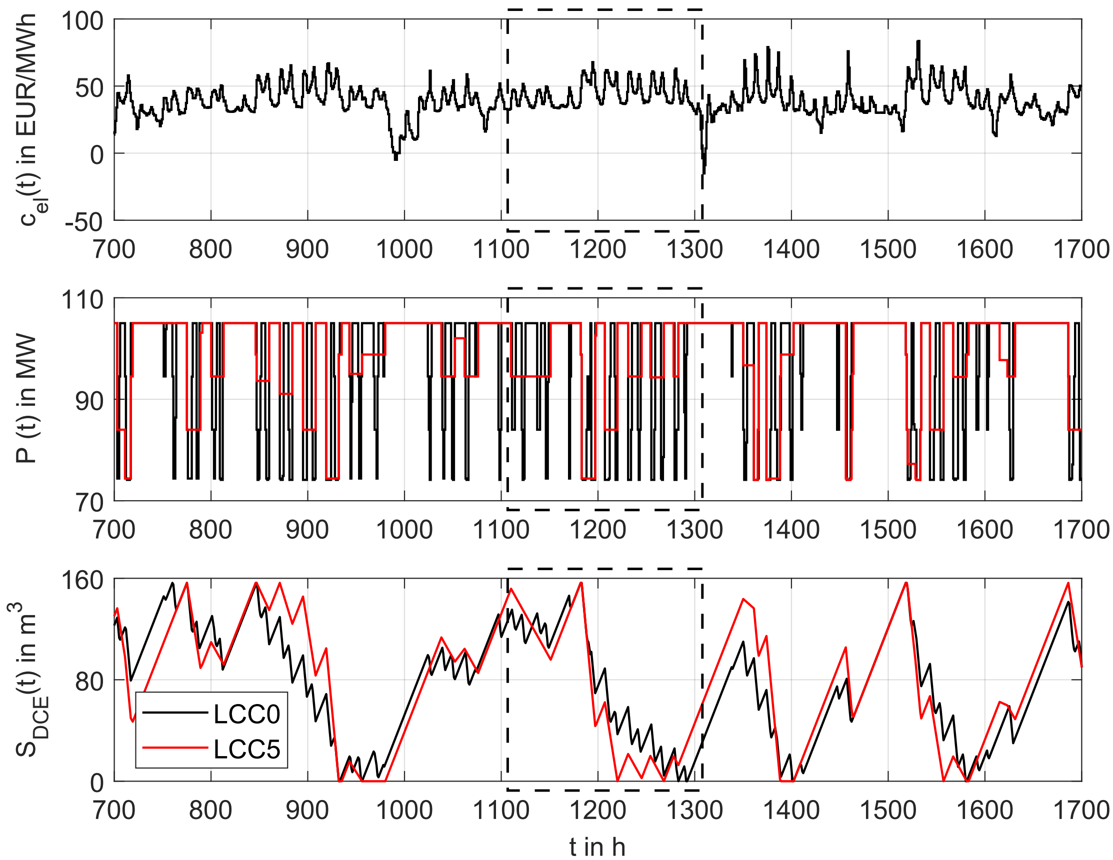

Figure 16: Results of operation scheduling for the power consumption $P(t)$ and the stored amount of DCE $S_{\mathrm{DCE}}(t)$ for different load change costs, i.e. $c_{\mathrm{LCC}} = €\,0$ per cycle (LCC0) and $c_{\mathrm{LCC}} = €\,5000$ per cycle (LCC5) in 2018 (exemplary section). The dashed squares mark the time horizon of the dynamic optimisation in the next section.

perform their own risk assessment at this point based on in-house methods and individual key performance indicators. In the next step, the practical feasibility of the identified operational trajectories must be verified to show that the obtained trajectories are not only economic, but also practically achievable.

4.3.3 Practical and realisable potential of DCE synthesis

Given the complexity of the dynamic process models and the increased computation times required to solve the respective dynamic optimisation problems, such models are not suitable to determine optimal operating policies over a longer time-horizon, e.g. a year. On the other hand, simplified models are often unable to determine how process parameters must be changed to allow for a flexible operation, due to their lack of detail. For this purpose, we selected a segment of 200 h for dynamic optimisation (marked by dashed boxes in Figure 16) to determine whether the trajectories obtained in the previous section can be realised in a real plant. This time period was chosen because it contained strongly varying loads. We only show results for the case with zero load change costs and assume that the less dynamic case with load change costs greater than zero will then also be feasible. Note that extended time periods with low or high load are automatically as only operating points within the window defined in Section 4.3.1 are allowed for flexible operation.

The assessment of the practical flexibility potential requires a dynamic model of sufficient detail. While steady-state and dynamic models for the chloralkali electrolysis were suggested by Wang *et al.*[103], Budiarto *et al.*[104], and Otashu and Baldea[17], we use our own dynamic models for CAE[101] and DCE production[100] as they have been validated with real process data applicable to the here investigated process concept. Both models are briefly summarised in the following paragraphs.

The CAE model describes catholyte and anolyte with independent mass balances. The ion exchange is described using empirical expressions that were fitted based on industrial plant data. The reaction rates for the production of Cl_2 and H_2 are expressed using Faraday's Law. In addition, the model contains a dynamic energy balance to assess the temperature by considering the convective flows of inlet and outlet, the enthalpy of reaction, the evaporation of water, and the input of electrical power. Finally, the model contains the heat exchangers and buffer tanks shown in Figure 15. Note that the possibility of an oxygen depolarized cathode is not considered here. The reader is referred to Brée *et al.*[15,16] and Roh *et al.*[98,105].

The model of the DCE production consists of dynamic mass and energy balances for the reactor, the distillation trays on top of it, and the reflux drum. Moreover, steady-state balances for the partial condenser and an external heat exchanger are incorporated. This external heat exchanger removes additional heat from the reactor. The manipulated variables of both models are presented in Table S4 in the Supporting Information together with their constraining parameters. More information on the specifics of the implemented models can be found in Weigert *et al.*[101] and Hoffmann *et al.*[100].

To assess the practical potential, the trajectory determined in the previous step is used in combination with the dynamic models of the plant over a period of 200 h. Over this time horizon, the optimal set points for all manipulated variables in both CAE and DCE production were computed by solving the optimisation problem given in Equation (7). In addition, the rate of load change is set depending on the active business option: the day-ahead market. As this business option does not require a specific load ramp, a ramp of 15 minutes is demanded at every set point change.

The CAE part is optimised in the gPROMS model builder v5.1.1[106], in which a ramp constraint is used to bound the slope of the manipulated variables. The parameters determining the ramp constraints and the weighting factors are given at the top half of Table S4. The DCE section is optimised in a Python / AMPL framework for which time is fully discretised via orthogonal collocation on finite elements[107]. This dynamic optimisation problem is solved by bounding the difference between the manipulated variables of two consecutive finite elements. The relevant parameters are given at the bottom of Table S4. The weighting factors in both objective functions were chosen so that all individual terms are approximately of the order of magnitude of 10^0.

Figure 17 and Figure 18 show the results under the demand response scenario developed in the previous section. As the models are based on industrial production plants, the data are normalised using their nominal set points, i.e. a value of 1 corresponds to the nominal value of a particular variable.

Figure 17 demonstrates the feasibility of the load trajectories, obtained during the assessment of the economic potential, for the CAE. The product flows of both caustic soda and Cl_2 are shown at the top. The produced chlorine is then used as feed stream for the DCE production. The cell temperature and both anolyte and caustic soda composition (mid) can be kept at their respective set points with virtually no deviation. The optimal trajectories of the corresponding manipulated variables (bottom) mimic the specified load trajectory. All manipulated variables deviate from their nominal value by a maximum of around 25 % while maintaining their specified change rate of 1 K min^{-1} and 15 nom.% min^{-1}.

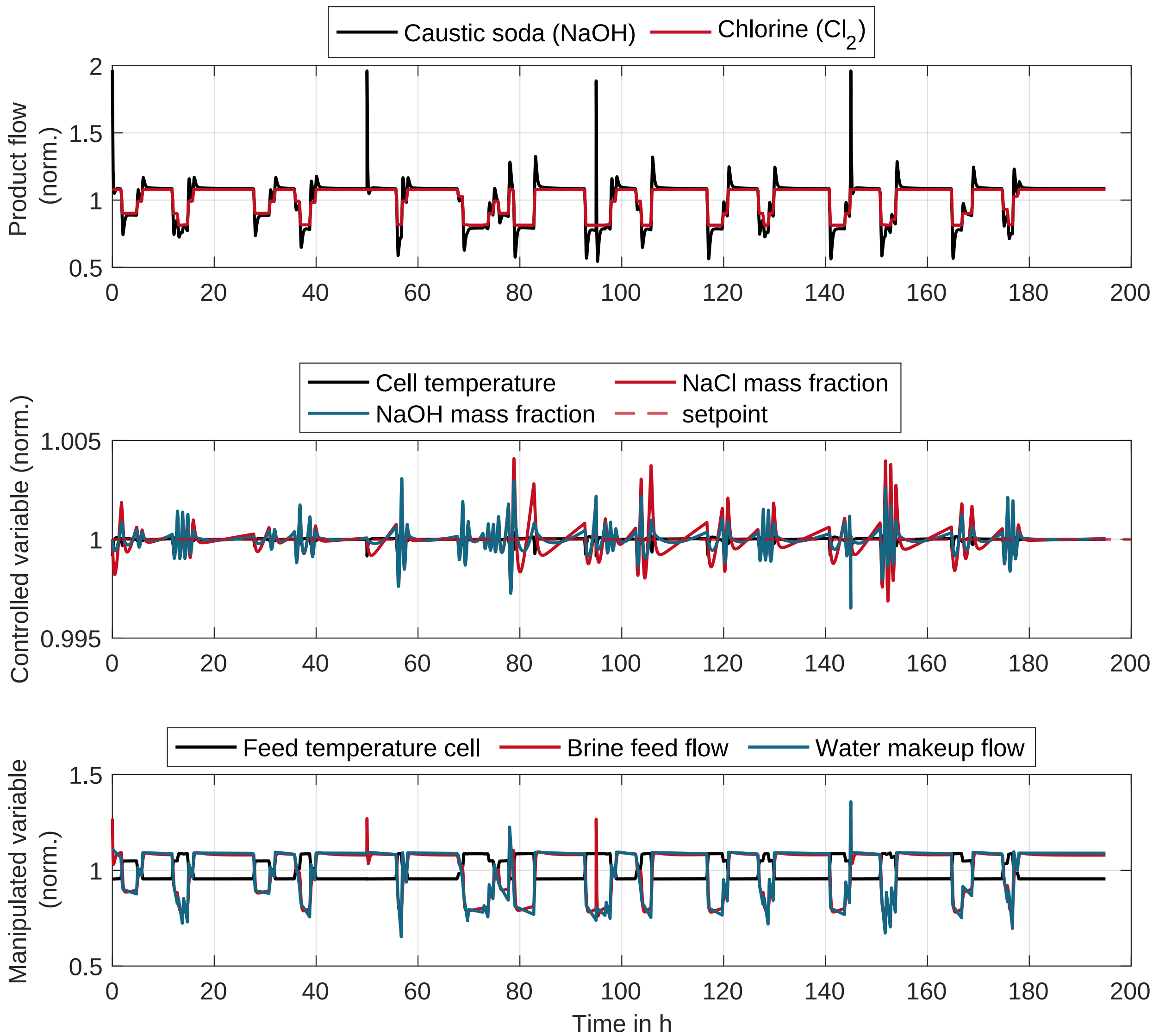

Figure 17: Results of dynamic optimisation for CAE to assess the practical potential. Top: Product flows of chlorine and caustic soda, normalised using their respective value at nominal load. Mid: Control variables of optimal control, normalised based on the corresponding set point. Bottom: Manipulated variables of the optimisation, normalised using their respective value at nominal load.

Figure 18 demonstrates the feasibility of the dynamic profiles for the DCE production.

Preferably, ethene follows the chlorine feed, thereby maintaining the required ethene excess of 10 % (top). Also shown is a comparison for the product flow between the operation model and the dynamic process model. Contrary to the OM, the DynOpt does not change these flows instantaneously but is restricted by the control constraints. As there is no significant difference in the integral mean of these two profiles, the storage constraints in the operation model hold. At the same time, the dynOpt ensures that the process remains operable by keeping the level in the reflux drum and reactor and the product concentration as constant as possible (mid). By also determining how the other manipulated variables must be modified to set the desired flows while maintaining product concentration, the dynOpt goes beyond the level of detail in the operating model. The time profiles of the manipulated variables are shown at the bottom of Figure 18. The heat removal at the bottom, intended to remove a part of the reaction enthalpy from the process, decreases whenever the gas load increases, and vice versa, to maintain a constant liquid holdup in the reactor and simultaneously increase (or decrease) the product flow. In addition, the reflux increases in times of larger loads. The control profiles obtained remain feasible but the heat flow reaches its upper limit (1.3 times the nominal value) on several occasions. This does not pose a restriction on the profiles computed in this contribution but may lead to a loss of feasibility for other business options.

These results allow for the assessment of the practical potential of the DCE production. As the economic assessment and the dynamic optimisation revealed no additional constraints, the practical potential is equal to the technical potential in this case (5 % for negative DR and 25 % for positive DR, business option: day-ahead market). This entails cost savings between 1 and 1.3 Mio. € per year, depending on the actual year and whether load change costs are considered. Note that there is no generic potential for DR response for a specific electrochemical process. Instead, its potential depends on the considered business options.

The results could serve as a base case for an additional loop according to Figure 3. In this loop, which goes beyond the scope of this case study, the plant design would be changed by extending the plant's capacity or the storage capacity. This would require the additional

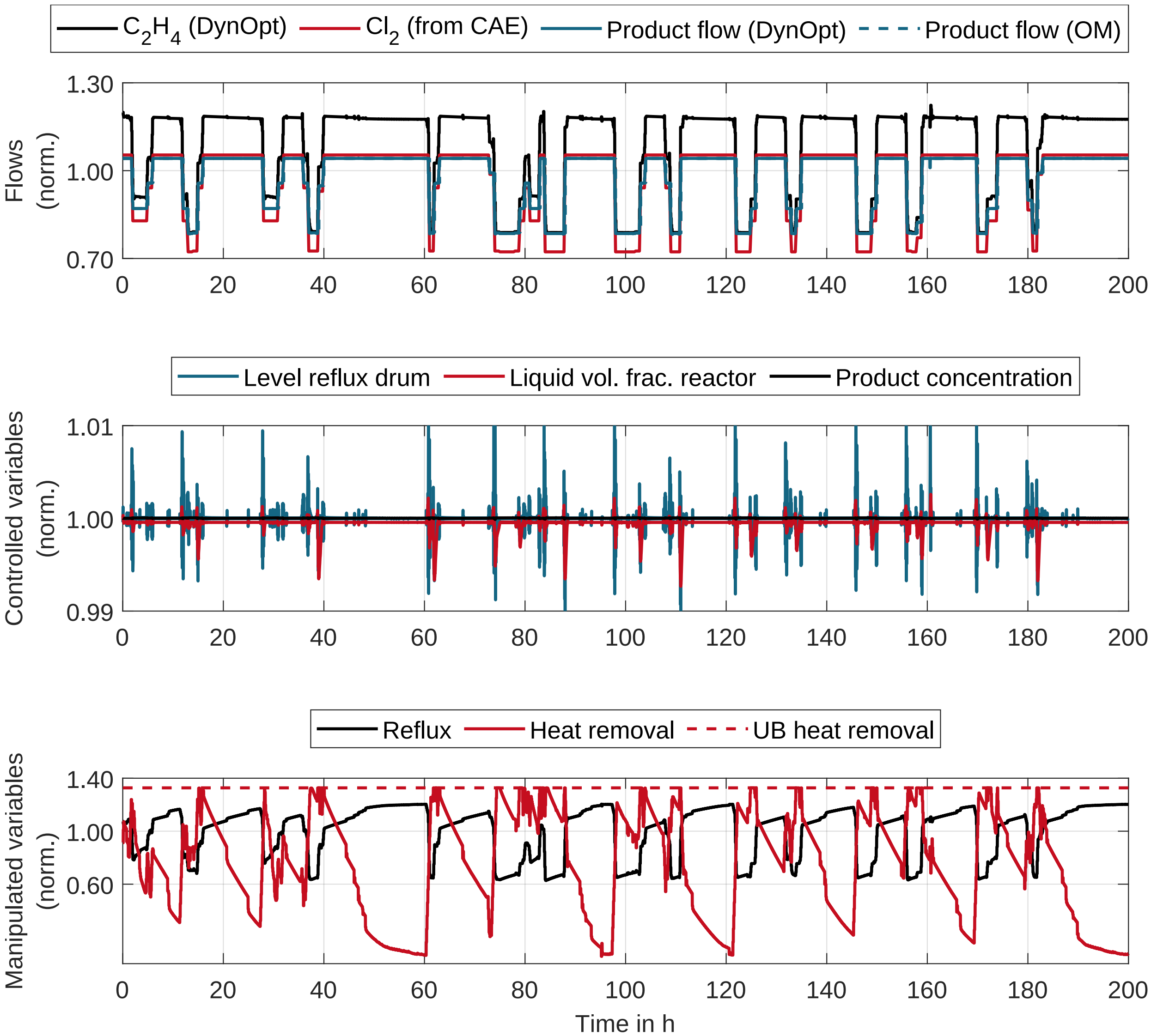

Figure 18: Results of dynamic optimisation for DCE production to assess the practical potential. Profiles obtained by dynamic optimisation are marked with DynOpt while trajectories determined with the operation model are marked OM. Top: Feed and product flows. Mid: Controlled process variables. Bottom: Manipulated variables of the optimisation. All variables were normalised using their respective value at nominal load except for the ethene feed, which was also normalised using the nominal chlorine feed.

investment costs to be considered in the assessment of the economic potential. For this new design, the practical potential would also have to be re-assessed to compare the current plant and the possible economic advantages of a capacity increase.

4.4 Critical analysis of the methodology

While the previous case studies have illustrated the methodology in more detail, we have so far not addressed why such a methodology is indeed helpful for determining the realisable potential for DR. For this purpose, recent research on the CAE was analysed to determine which fundamental aspects of our methodology were included in these contributions. The results of this comparison are shown in Table S5 in the Supporting Information in which we differ between scheduling models and rigorous dynamic models combined with dynamic optimisation. First of all, we note that control and ramp constraints are not usually considered in scheduling models as they often do not even incorporate the inherent manipulated variables. They also usually neglect process dynamics completely, so even if ramps for load changes were considered, this would not show operation challenges in the actual plant. Contrarily, not every contribution actually considers an allowable load range although this has a decisive impact on the economic potential. As this is such a vital part during the assessment of the economic potential, we included the determination of the operating window in the prior step. This also helps in identifying bottlenecks for flexibility at an early state.

The most relevant key figure are, however, the costs. Unfortunately, the list of considered terms in the objective function varies notably. Based on the results of case study 3 and Table S5, the following conclusions can be drawn:

1. Profits from product streams should not be considered for applications in the electrochemical industry because the customer's demand must be satisfied in any case. A company could of course adjust its production in case of a promising business option for flexibility, but such a decision would have to be made on the logistics level in the decision process and not on the scheduling level

2. Scheduling models typically consider electricity costs, additional income due to balancing services. Occasionally, investments costs for increased plant or storage capacity is considered. However, the additional load change costs are rarely considered or even quantified. This is particularly relevant as we could show that these costs strongly influence the number and amplitude of load changes (Figure 16)

The fact that load change costs are still unknown, even for a very mature technology such as CAE, caused us to contemplate when such data would have to be compiled. At this point, the relevance of extended flexibility experiments to determine long-term damage on materials became obvious. The results of such experiments will generate estimates for how strongly load changes reduce service life of components. At the same time, we acknowledged that the determination of material stability during flexible operation only makes sense if the process may be operated reliably at steady-state. Therefore, we coupled flexibility experiments to the TRL of the process. This way, the methodology was developed backwards.

The few studies with rigorous models have so far integrated the economic and the practical analysis. According to our methodology, these two potentials are independently determined as the the load profile is fixed for the assessment of the practical potential. Moreover, the impact of control and ramp constraints has hardly been studied. It is often not considered that an electrochemical profile must follow a carefully defined load profile during load changes and that manipulated variables cannot arbitrarily be changed. For this reason, this was added explicitly to our methodology to ensure that the process may be operated flexibly while following the load ramps of the respective business option.

In summary, it is assumed that the realisable potential of another electrochemical process can be identified much faster in the future due to the developed methodology given that the individual steps are now connected in a systematic manner. Nevertheless, three major challenges still must be addressed in future research: First of all, the incorporation of different business options must be improved. Currently, two different business options are assigned individual load ranges, e.g. 10 MW for mFRR and 1 MW for FCR. Here, more systematic methods to determine the individual load ranges would be desirable. Secondly, the solution of the scheduling process is still deterministic – the electricity price is known a priori for the whole time horizon and the optimisation algorithm may balance operation in an unrealistic way. To address this issue, we propose to solve the scheduling problem with a moving-horizon approach. This will decrease problem size and therefore computational effort significantly and at the same time yield more realistic results. Lastly, FCR may not yet be considered in the dynamic optimisation problems because its fluctuations occur at a much higher frequency than other load changes. This may be addressed in the future by considering the FCR as an uncertain parameter and solving a stochastic, dynamic optimisation problem to determine trajectories that are feasible under such highly frequent fluctuations.

5 Conclusion and Outlook

This contribution proposed a methodology to assess the realisable flexibility potential of (electro-)chemical processes for DR applications. The first decision variable in this methodology is the technology readiness level of the investigated process: If the TRL is below Level 8 or flexibility experiments are not readily available, the theoretical potential is determined. For a TRL below 6, more fundamental research is required to allow for stable process operation. Otherwise, a SWOT analysis is carried out to evaluate a possible application, e.g. by comparing the process to other alternatives. If a benefit of this process can be identified, flexibility experiments are carried out to determine whether continuous fluctuations have an impact on selectivity and material stability, which is an important precondition for the cost quantification later on.

For a TRL greater than or equal to 8, the whole process flowsheet must be analysed to determine the operating window in a flowsheet analysis. The analysis must consider various criteria regarding reaction, process, and control engineering, such as sensitivity of conversion or selectivity, and availability of reactants. The flowsheet analysis results in a flexibility categorisation between A and D and a categorisation of load range between 1 and 3. Highly desirable are processes in the category A1, i.e. their flowsheet revealed negligible barriers for flexible operation and they offer a large load range. Afterwards, a simplified model for operation scheduling is set up to determine the economic potential based on the possible business options by solving an optimisation problem, which yields realistic load profiles and product flows. Should a relevant economic potential be determined, dynamic optimisation based on rigorous dynamic process models is used to determine whether the trajectories obtained in the previous step are feasible. This yields the realisable flexibility potential of the investigated process.

The proposed methodology was applied to three case studies of varying TRL. In case study 1, we investigated the electrochemical production of H_2O_2 in acid media, which has a TRL below 6. The case study was chosen to illustrate that conventional processes can potentially be replaced by electrochemical processes, which are then able to participate in flexibility markets. We showed that the addition of small amounts of K_2SO_4 significantly enhances the efficiency of this process. While the Faraday efficiency in 0.1 M H_2SO_4 is appreciably lower than for 0.1 M KOH, the addition of 0.05 M K_2SO_4 decreases the further reduction of H_2O_2 to H_2O in acidic media and thus increases the Faraday efficiency above its value in alkaline media. This represents an important step in the identification of the optimum process conditions in acidic media. However, there is still further research required regarding the stabilising agent and the cell material, but also with respect to the overall process concept, to elevate the TRL in the future. In this context, we pointed out the advantages of collaborative, interdisciplinary research of electrochemists, process, and energy engineers to reduce potential bottlenecks for flexible operation right at the beginning.

In case study 2, the electrochemical hydrodimerisation of acrylonitrile was studied for various load profiles. So far, no significant disadvantages in terms of selectivity could be observed after repeated load changes. In fact, the yield was improved compared to the corresponding yield at a constant current density, although this has to be validated by further experiments. The limits of flexibility for this process must be found by increasing the rate of load change v_P and tuning the duration of the load change t_P. As a next step, long-term experiments will give more insights into the stability of the cell components and thus allow for an estimation of the associated load change costs.

Finally, case study 3 presented results for the chloralkali electrolysis in combination with the synthesis of 1,2-dichloroethane. Following the methodology, we initially determined the operating range using a flowsheet analysis. Then, an economic optimisation was carried out, in which electricity was purchased at the day-ahead market. The solution of this optimisation problem yielded economic trajectories, which were then applied on validated dynamic process models to determine feasible control profiles via dynamic optimisation. Importantly, the optimisation problem also considered bounds for control changes. The results showed the process to have a realisable potential for DR of 25 % of the nominal load (positive) and 5 % of the nominal load (negative). In this particular case, this equals the technical flexibility potential of the process.

Future research will focus on developing more quantitative criteria for the ratio between business options, formulating the operating model as a moving-horizon problem, and integrating quickly fluctuating business options, such as FCR, in the dynamic optimisation problem.

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Supporting Information Available

Supporting Information is available for this manuscript, which contains the

- operating conditions of case study 1
- operating conditions of case study 2
- results of the flowsheet analysis of case study 3
- weighting factors and control constraints for case study 3
- comparison of various publications regarding the considered costs as well as control and ramp constraints for case study 3.

This information is available free of charge via the Internet at `http://pubs.acs.org/`.

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Graphical TOC Entry