


Assessing the Realizable Flexibility Potential of Electrochemical Processes

Christian Hoffmann,* Jessica Hübner, Franziska Klauke, Nataša Milojević, Robert Müller, Maximilian Neumann, Joris Weigert, Erik Esche, Mathias Hofmann, Jens-Uwe Repke, Reinhard Schomäcker, Peter Strasser, and George Tsatsaronis

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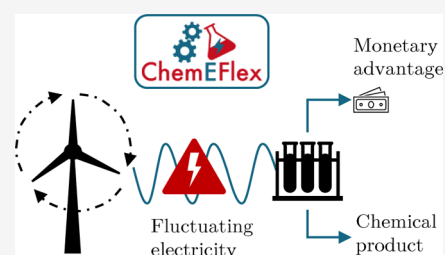
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ABSTRACT: Demand response is a viable concept to deal with and benefit from fluctuating electricity prices and is of growing interest to the electrochemical industry. To assess the flexibility potential of such processes, a generic, interdisciplinary methodology is required. We propose such a methodology, in which the electrochemical fundamentals and the theoretical potential are determined first by analyzing strengths, weaknesses, opportunities, and threats. Afterward, 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 flow sheet analysis, the formulation and solution of a simplified model for operation scheduling under various business options, and a dynamic optimization 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.



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 optimized for a specific production capacity to minimize 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 for example, exploitation of varying electricity prices or financial compensation for providing grid balancing services (BSs). 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, either plants are operated at high capacity in the case of low electricity prices and at low capacity in the opposite case^{5–8} or a load reduction/increase is offered to the transmission system operators (TSOs) for stabilizing 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 utilizing price signals.^{12,13} Many technologies and processes have been analyzed in more depth concerning DR applications, including wastewater treatment,¹⁴ chloralkali electrolysis (CAE),^{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, that is, the actual available and realizable load change, of DR for electrochemical processes. Only Dranka and Ferreira²³ 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 Ferreira²³ do not give any details on how to quantify the potential and which specific steps

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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 to assess, for example, 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 and 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, that is, 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 optimization as suggested by Grossmann and Floudas²⁹ 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 DR and possibilities for load management as well as the subcategories of flexibility potentials. Section 3 presents the proposed methodology to assess the realizable flexibility potential. Within this methodology, every potential type, that is, 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 processes of varying technology readiness levels (TRLs): 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 the results relevant for identifying appropriate process parameters in preparation for their implementation in a mini-plant. Second, we present the 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. Third, we analyze the CAE 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 realizable potential, which include a detailed analysis of the flowsheet (FS), the description of the costs associated with DR, the solution of an optimization-based scheduling problem, and the solution of a dynamic optimization 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 DR as synonyms, we follow the following broader definition for the former:

Definition 1 (Demand-Side Management³¹): *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, that is, 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.

DR 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 Response³²): *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 a 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 a 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, the CAE has an average annual capacity utilization 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 (Flexibility³⁵): *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.*

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 Pehnt³⁶ or Gils.³⁷ However, there is yet no uniform classification. We adopt the definition given by Klauke et al.³⁸ and extended by Ausfelder et al.,³⁴ with five subcategories, namely, theoretical, technical, economic, practical, and realizable potential (Figure 1).

The theoretical potential describes the maximum possible flexibility that is available for a chemical process. It is computed

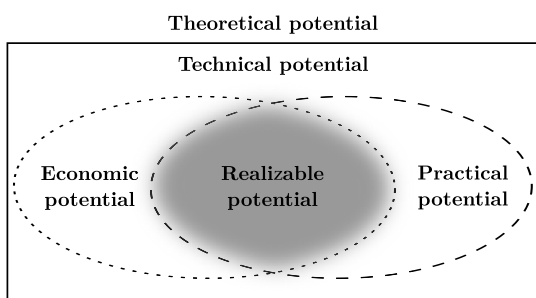


Figure 1. Types of flexibility potentials and their relation for (electro)chemical processes based on Klaucke et al.³⁸ and Ausfelder et al.³⁴

either from the installed capacity of a specific process (in case we evaluate an established process with $\text{TRL} \geq 8$) or from the capacity estimated to satisfy the market demand (in case we evaluate a process still in development with $\text{TRL} < 8$). 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 electrolyzer cell or 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, for example, 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, for example, ramp constraints for which the transient plant trajectories must remain feasible in specific DR scenarios and markets. This way, not only the plant's capability to operate at reduced load is ensured but the plant is also capable of achieving this operating mode safely, efficiently, and within these specific time constraints. The intersection of economic and practical potential yields the realizable potential. Only this potential could be realized economically by a company while adhering to constraints for product purity or control changes. However, most studies determine either the theoretical potential³⁷ or the technical potential³⁴ because much expertise and process knowledge are required to assess the limitations of a specific process.

2.2. Parameters Determining the DR Potential. Load change scenarios are characterized 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 realized as a ramp and does not occur instantaneously. The rate of a load change dP per time period dt 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.

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

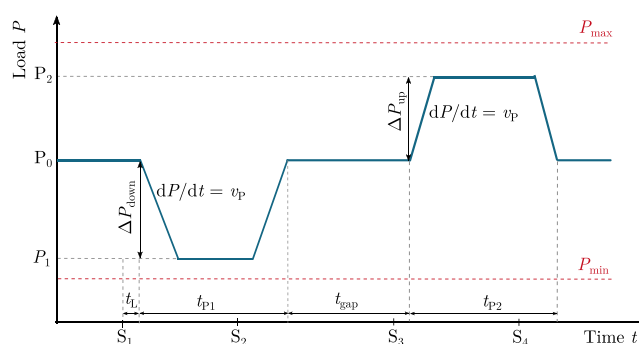


Figure 2. Schematic load profile to illustrate the parameters for assessing the practical potential of DR. Linear load changes are depicted for simplification and do not necessarily represent reality. ΔP : load change; v_p : rate of load change; t_p : duration of load change; t_{gap} : time gap between 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.

Latency: The parameter t_L describes the delay between the signal s to initialize 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. Either the parameters can be given by process constraints, for example, the minimum load, or they are determined by a particular business option, for example, 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.

3. METHODOLOGY

The proposed methodology to assess the realizable flexibility potential of an electrochemical process is presented in Figure 3. First of all, we distinguish between electrochemical fundamentals as well as theoretical potential (left branch) and industrial application (right branch) using the TRL. The TRL describes the maturity of a technology. There are nine levels, with one being the lowest and nine the highest.³⁹ Although originally introduced for the space travel technology, TRL has also been applied in the chemical industry, for example, 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.

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

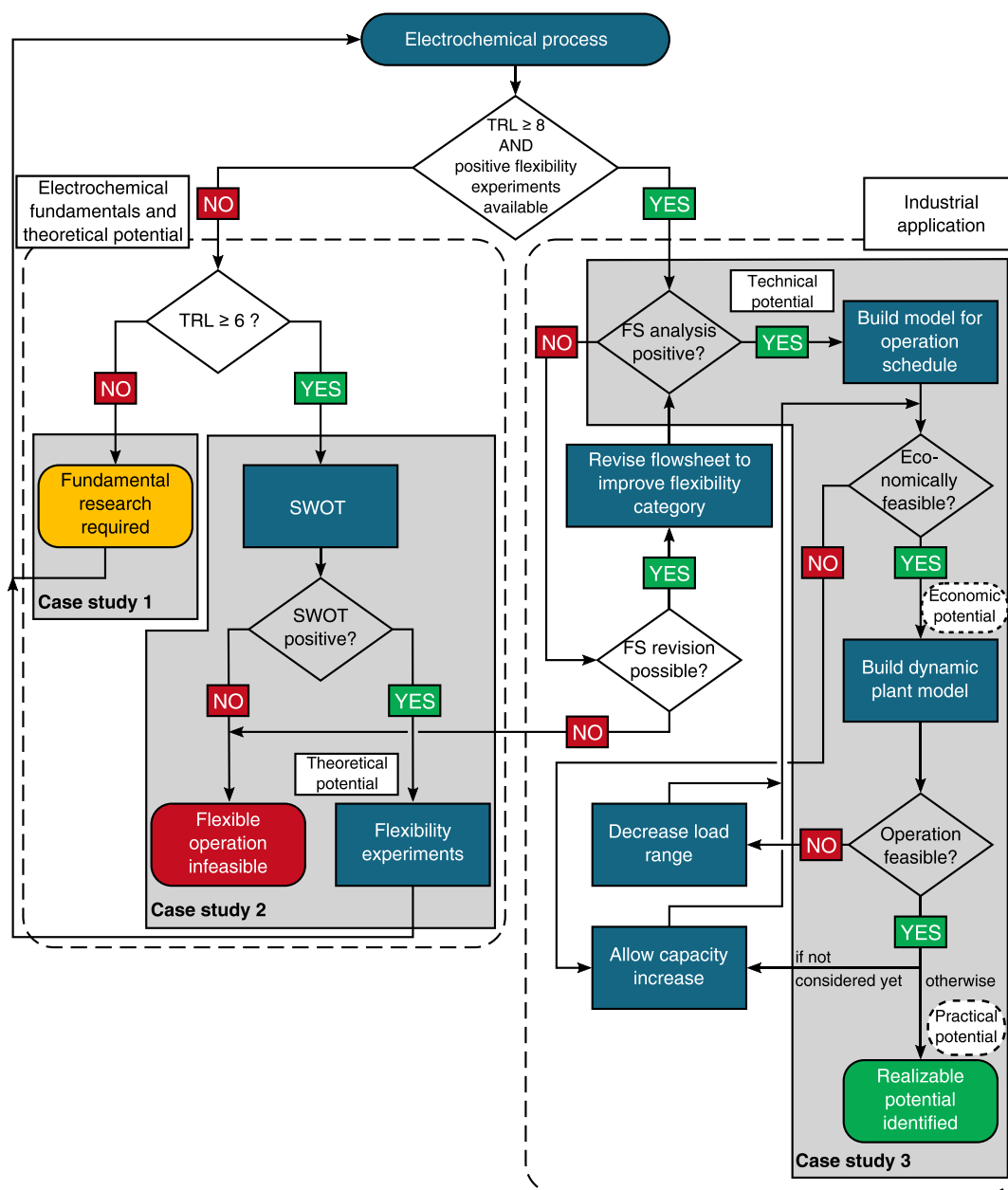


Figure 3. Proposed methodology to assess the realizable flexibility potential of an electrochemical process. TRL: technology readiness level; SWOT: strengths–weaknesses–opportunities–threats; FS: Flowsheet. The blocks mark which methodology steps are covered in each of the three case studies.

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 the 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 given possible competitors and process alternatives.

The investigated criteria for this attempt are:

- Product market size and product market development
- 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 weigh each category or even define exclusion criteria, that is, 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

Table 1. Description of TRL Applied in the Chemical Industry, Adopted from Buchner et al.⁴⁰ and Shortened for This Work^a

TRL	title	tasks
1	idea	identification of opportunities
2	concept formulation	technology concept/application, patent research
3	proof of concept	experimental research in the laboratory, qualitative observation of predicted reaction
4	preliminary process development	experimental concept validation, scale-up experiments, conceptual process design
5	detailed process development	formulation of the shortcut model
6	pilot trials	construction of the mini-plant/pilot plant
7	final engineering	performance optimization for the pilot plant
8	commissioning	integration of products and processes into the organization structure, construction of the full-scale plant
9	production	audit of the full-scale plant

^aSee original work for the extended version.

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 nonelectrochemical 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 determine 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, for example, 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 the converted reactant into the desired product under consideration of the stoichiometry

$$S_p = \frac{n_p \cdot (-\nu_E)}{(n_{E,0} - n_E) \cdot \nu_P} \quad (1)$$

where n_p is the amount of the desired product, ν is the corresponding stoichiometric coefficient, $n_{E,0}$ is the amount of reactant E before the reaction, and n_E is 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 $n_{E,0}$ under consideration of the stoichiometric coefficient ν

$$Y_p = \frac{n_p \cdot (-\nu_E)}{n_{E,0} \cdot \nu_P} \quad (2)$$

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

$$r = \frac{n}{A_{\text{Geo}} \cdot t} \quad (3)$$

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

$$FE = \frac{z \cdot c \cdot V \cdot F}{Q} \quad (4)$$

where z is the number of transferred electrons, c is the concentration of the product, V is the electrolyte volume, F is the Faraday constant, and Q is 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 Applications 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 an 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. In terms of process engineering, the following aspects are deemed relevant.

Electrochemical Cell: State-of-the-art membranes for electrolysis are designed for low electrical resistance, high selectivity toward the preferred ion transport, and high chemical resistance against aggressive conditions in the electrolytes. To meet these requirements, there is in general only a small operation window of the electrolyzer 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 favor 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 CAE 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, for example, 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. Second, the number of downstream process units between the electrolyzer and storage tank is relevant: the more units are part of the FS, the more units must operate flexibly. Their number is thus an indicator of how easily the process could be operated flexibly. Third, 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, that is 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 could 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 sale 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 a low environmental impact if released,
- not be highly toxic or highly reactive (preferably nontoxic and nonreactive), and
- 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, for example, 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 plant control and 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 stabilization 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 the feed amount and composition may also influence 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 our simplified approach generates reasonable limits for operation.

3.3.3. Categorization. The relevant aspects for the FS analysis are summarized 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 Klauke et al.,⁴⁷ the flexibility category of the whole process is set to the lowest of all subcategories. Note that the categorization 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 categorization of the operating window, but it illustrates how such a categorization can be made.

We rank the storability of products or intermediates according to the criteria outlined above. Although a more quantitative analysis would be favorable 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 weighed against each other. In addition, safety regulations and requirements may vary from country to country. Hence, internationally valid chemical classifications⁴⁸ should be consulted, and the storability of chemicals should be discussed with safety engineers in practice. 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 CAE as only a few processes in the chlorine value chain can actually be

Table 2. Flexibility Categorization and Categorization of Load Range Based on FS Analysis, Extended from Klaucke et al.⁴⁷

aspect	criterion	flexibility categorization (A, B, C, D)	
Process Engineering			
electrolyzer	damage to the membrane or electrodes	none, mild, strong, severe	
subsequent units	restrictions for heating/cooling	yes or no	
	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	additional limitations?	
	heating/cooling	at which load?	
	peripheral processing steps		
storability of the product	state under ambient conditions	solid/liquid or vapor?	
	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 the electrolyzer and subsequent units	categorization of load range (1, 2, 3)	
P_{\min} , P_{\max}	maximum load reduction with respect to P_0	>20%; 5–20%; <5%	
	maximum load increase with respect to P_0	>10%; 5–10%; <5%	

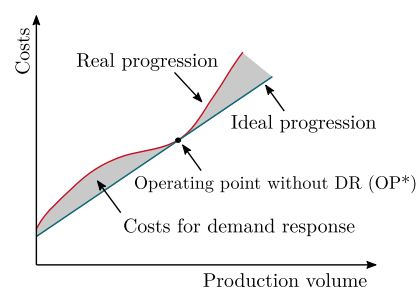
operated flexibly.⁴⁷ This may help in focusing on the most relevant processes for flexible operation. The FS analysis in Figure 3 thus specifies which processes actually offer technical potential for DR and should be further evaluated regarding their economic potential (category A). Category B (and potentially category C) may go through a re-design step in which the FS is modified to remove the bottlenecks for flexible operation by adjusting process design or the control scheme. If an FS 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 categorization 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 categorization consists of the combination of the flexibility category and the load category, for example, A3, which would indicate a process with excellent properties regarding process stability and product storability, but a very limited load range. This numeral category may help when selecting appropriate business options in the assessment of the economic potential (the next step in the methodology). For example, a process of category A3 would—as a first approach—primarily operate in markets with a small load range but a 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. Second, these costs are related to the remaining DR parameters. Finally, a suitable model for operation scheduling is proposed.

3.4.1. Costs of DR. 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

**Figure 4.** Visualization of the costs of DR.

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 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 investment costs 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.

LCCs 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 the 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.

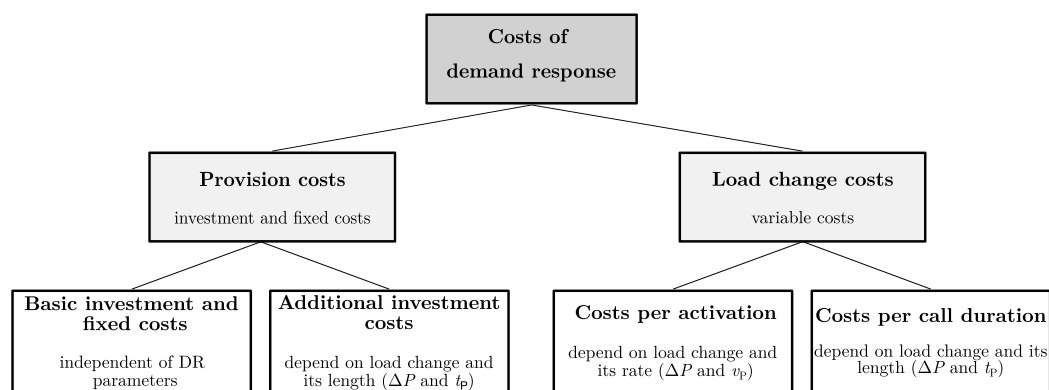


Figure 5. Classification of DR costs and their dependence on the DR factors.

Table 3. Summary of the Relevant Parameters of the German Reserve Market

	FCR	aFRR	mFRR
Function ⁵⁸	rapid stabilization of grid frequency after the 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		six time slices with a length of 4 h each	
payment	pay-as-cleared load price	pay-as-bid load price and price per MW h in the case of call	
Access Requirements (Prequalification) ⁵⁹			
latency	$t_L \leq 2$ s	$t_L \leq 30$ s	$7.5 \text{ min} \leq t_L^a \leq 22.5 \text{ min}^{60}$
complete activation	automatic, within 30 s	automatic, within 5 min	manual, within 15 min
rate of load change		$v_p \approx \Delta P / (\text{activation time})$; quasi-linear ramp for load change	
duration of load change	$t_{p,\text{max}} = 15$ min	$t_{p,\text{max}} = 20$ min	$t_{p,\text{max}} = 20$ min

^aValues for prequalification are not specified; typical values during operation are shown instead.

The costs per activation are more difficult to determine. At this point, long-term stability investigations as proposed in the left branch of our methodology become relevant: by comparing experimental results obtained for steady-state operation to the results for flexible operation, the impact of fluctuating inputs can be quantified. In combination with known costs for renewing degraded process equipment, this allows a good estimation of the costs per activation. Such an approach is illustrated by Hofmann et al.,¹⁹ who estimate the LCC for the CAE. 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 this later on via dynamic optimization 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 organized differently in every country and continuously changes to adapt to current challenges. Albadi and El-Saadany⁵⁴ classified existing DR programs. They found that the option with minimum effort for DR-to-market is currently optimization 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 5 min before the actual supply.⁵⁵

Another business option is the participation in DR programs of the TSOs, such as control reserve markets or capacity markets. These markets aim at stabilizing 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 summarized capacity markets for most European countries and the United States. Currently, an initiative supported by the European Network of TSOs for Electricity (ENTSO-E) standardizes 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 summarized 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 4 h without the possibility of intervention by the process operator. Therefore, the time between two load changes t_{gap} may be 0.

3.4.3. Model for the Operation Schedule. To determine the economic potential of DR, it is necessary to consider the monetary advantage of flexible plant operation compared to nonflexible operation that results from the utilization 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, the economic evaluation should be done for a sufficiently long time period and for different market scenarios, for example, 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 optimization. The operation scheduling model provides the optimum time profile of the consumed electrical power and the respective production quantity. The solution will depend on the input, for example, fluctuating power price time series, and must consider 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 optimization problems (NLP, MINLP) are often 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 us¹⁹ 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 behavior, a simplification of the problem is possible, for example, by using piecewise linearization. The resulting (mixed-integer) linear optimization 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 LCC, plus the provision costs as shown in Figure 5:

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

$$\text{s. t. } 0 = g(\dot{V}_{\text{Prod}}, P, S, t) \quad (\text{simplified process model}) \quad (\text{5b})$$

$$P_{\text{min}} \leq P(t) \leq P_{\text{max}} \quad (\text{load constraints}) \quad (\text{5c})$$

$$0 \geq S(t) - S_{\text{max}} \quad (\text{storage constraint}) \quad (\text{5d})$$

$$S(t_{\text{start}}) = S(t_{\text{end}+1}) \quad (\text{optional: load shift constraint}) \quad (\text{5e})$$

This scheduling task is formulated as a time-discrete, nonmodal optimization problem as has been done in prior

research.⁶⁴ Other problem formulations can, for example, be found in Floudas and Lin⁶⁵ or Obermeier et al.⁵³

In the stated optimization problem, only P_{min} and P_{max} must be specified according to the boundaries identified in the FS 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 BS, are considered, the resulting income is subtracted from the cost and additional constraints have to be introduced:

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

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

$$P_{\text{min}} \leq P(t) \leq P_{\text{max}} \quad (\text{load constraints}) \quad (\text{6c})$$

$$0 \geq S(t) - S_{\text{max}} \quad (\text{storage constraint}) \quad (\text{6d})$$

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

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

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

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

The difference between the current load and maximum/minimum load of the plant limits the volume of available BSs. In eqs 6e and 6f, the quantities $P_{\text{neg.BS}}$ and $P_{\text{pos.BS}}$ account for a 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 a large economic potential) than options with lower v_p and ΔP . A starting point to consider this may be the load category identified in the FS 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 realizable) 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.

3.5. Practical and Realizable 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 the 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, that is, 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 appears reasonable from the standpoint of practical applications: 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 optimization. In case an economic potential is determined, the dynamic optimization can be set up.

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

$$\min_u f(u, x) = \sum_i \phi_i f_i \quad (7a)$$

$$\text{s. t. } 0 = g(u, x, \dot{x}, P, v_p, t) \quad (\text{dynamic process model}) \quad (7b)$$

$$0 \leq h(u, x, P, v_p, t) \quad (\text{path constraints}) \quad (7c)$$

$$u_{\text{LB}} \leq u \leq u_{\text{UB}} \quad (\text{absolute control bounds}) \quad (7d)$$

$$0 \geq \left| \frac{du}{dt} \right| - \dot{u}_{\text{max}} \quad (\text{ramp restrictions}) \text{ or} \quad (7e)$$

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

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 orders of magnitude, it is necessary to normalize these deviations with the nominal value of the respective variable. Other recent advances in the area of dynamic optimization, 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 optimization 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 Δu_{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 the continuity condition). Both Δu_{max} and \dot{u}_{max} must be set to realizable 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 optimization problem.⁶⁸ This approach has also been used in the context of DR²¹ 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 the results obtained from optimization. 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 optimization, 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 recomputed 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, for example, 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, that is, 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 realizable flexibility potential of an electrochemical process has successfully been assessed. This realizable 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 emphasize the methodology's interdisciplinary approach toward research in DR:

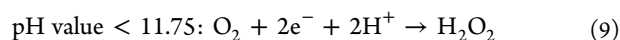
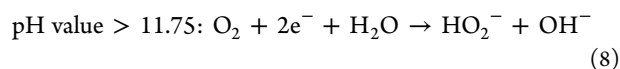
1. Case Study 1: Research on electrochemical processes may allow for the substitution of conventional nonelectrochemical processes in the future, thus creating new flexibility markets.
2. Case Study 2: Flexibility experiments on the lab scale assist in identifying the impact of flexible operation on selectivity and yield and will allow 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 catalyzed 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 DR, 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, an expected demand increase of 3.5% over the next 7 years⁷²) 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 engineers, 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 (eqs 8 and 9). A more detailed overview of the different reaction mechanisms can be found in Yeager.⁷⁶



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 available⁴⁰ (Dow-Huron Cells^{77,78}), but the high alkalinity of the product limits its application because alkaline H_2O_2 solutions 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 and their TRL is 3–4⁴⁰. According to Figure 3, this requires more fundamental research to determine suitable reaction and process parameters 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

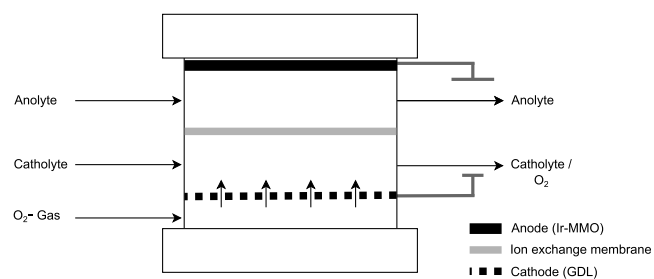


Figure 6. Schematic structure of the micro flow cell.

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 attached to carbon fibers. The experimental conditions realized 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 as a function of the current density CD 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 7a). 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 7b. 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 minimize 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 the lowest for 0.1 M $\text{H}_2\text{SO}_4 + 0.05$ 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 medium, the next steps to complete TRL 4 will require a larger set of reproducible data points to demonstrate the proof of concept on the 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

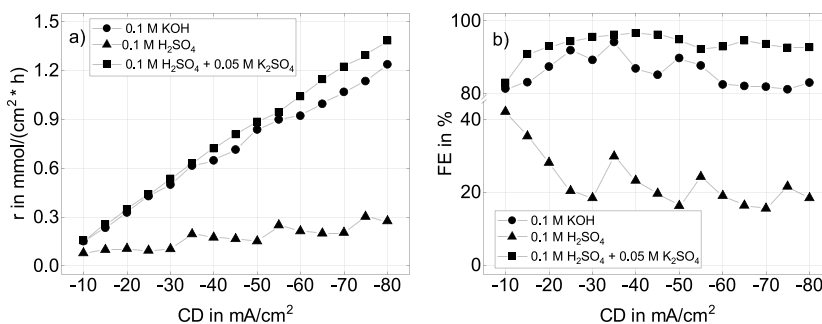


Figure 7. (a) Production rates and (b) Faraday efficiencies for 0.1 M H₂SO₄, 0.1 M KOH, and 0.1 M H₂SO₄ + 0.05 M K₂SO₄.

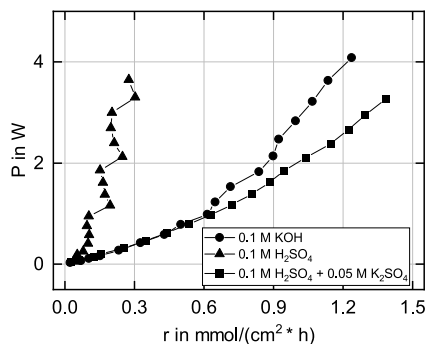


Figure 8. Power consumption P for 0.1 M H₂SO₄, 0.1 M KOH, and 0.1 M H₂SO₄ + 0.05 M K₂SO₄.

processes on the 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 FS 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 (ADN) 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}

Adiponitrile is an intermediate product that is further processed to Nylon-6,6 fibers 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 ACN.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 1960s⁸⁹ and the Japanese company Asahi Kasei.⁹⁰ To increase the economic efficiency, both companies eventually developed a synthesis process with undivided cells⁹¹ whose typical operating conditions are shown in Table S2 in the Supporting Information. The reaction takes place in a two-phase electrolyte, in which the organic phase consists of ACN and the products, while the aqueous electrolyte contains a mixture of quaternary ammonium salts and phosphate salts.

The reaction mechanism of the electrochemical reaction of ACN to ADN has not been conclusively determined. A widely held view is the formation of two anionic intermediates, the ACN radical anion (B) and the dimeric radical anion species (C) (Figure 9).^{92–94} From B, both the byproduct 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, ADN. Other byproducts are also possible, but PN 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

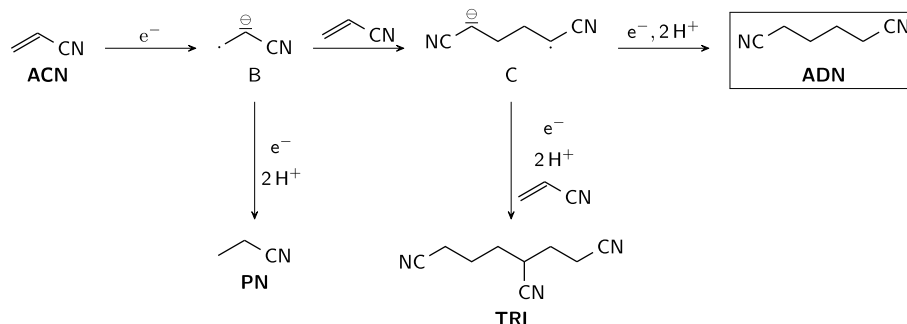


Figure 9. Reaction network of the cathodic electrohydrodimerization from ACN.

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	ACN and cadmium are harmful for health and the environment
only one synthesis step instead of three for the DuPont process ⁹⁵	O ₂ and H ₂ are produced at the anode and cathode, which is a potential safety risk ⁸⁹
oil and gas prices have low impact on process economics	electricity price has a larger impact
moderate operating conditions (atmospheric pressure, 55 °C) ^{86,94}	large carbon footprint when using electricity from fossil fuels
undivided cell yields a robust configuration. ⁸⁹	significant capital investments ⁸⁴
Opportunities	Threats
continuously high demand for nylon-6,6, which is currently not substitutable ⁸⁴	butadiene route is still more economically favorable, and competitors on the market are stronger
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	

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 favor 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 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 Hayati⁹⁶ 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 current is controlled with a potentiostat (11). The electrolyte temperatures 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 ACN vapor is condensed using a reflux condenser (5), while noncondensable gases produced at the electrodes may leave the system through the vent. A gear pump (9) feeds the electrolyte through a static mixer (10) 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 byproduct PN increases, while the formation of the trimer decreases. This is also in agreement with observations in the literature.⁹⁶ Furthermore, bis-cyanoethyl ether is observed

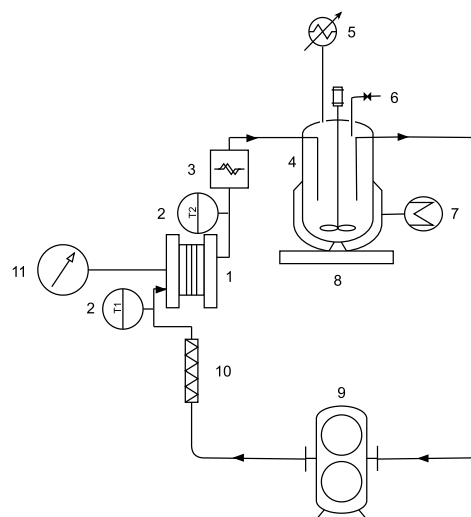


Figure 10. Setup for flexibility experiments for the electrochemical production of adiponitrile. (1): Parallel plate electrolysis cell, (2): thermocouples, (3): Coriolis flow meter, (4): electrolyte storage with a magnetic stirrer, (5): reflux condenser, (6): sample valve, (7): thermostat, (8): magnetic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

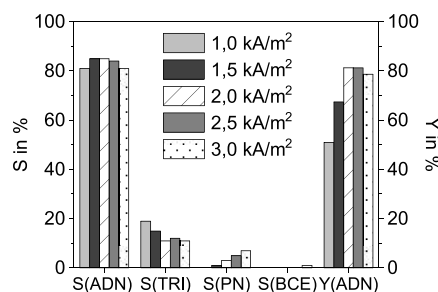


Figure 11. Selectivity toward ADN, the trimerization product (TRI), and PN and yield of ADN at a constant current density after 6 h of reaction time.

at a current density of 3 kA m⁻². The higher percentage of the trimer at lower current densities can be explained by the mass transport limitation in the system, which promotes oligomerization. The formation of PN at higher current densities is the result of a poorer current efficiency since injected electrons are also consumed by other reaction paths in the reaction network (see Figure 9).

Afterward, 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 min (Figure 12). The experimental data show that the selectivity toward adiponitrile as well as the activity hardly vary under this flexible operation. When increasing the current density after the reduction, the previously described kinetic 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 min 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 that for a constant load profile with the same average current density (1.5 kA m⁻²), as shown in Figure 14. Pulsation of the corresponding voltage could therefore lead to further improve-

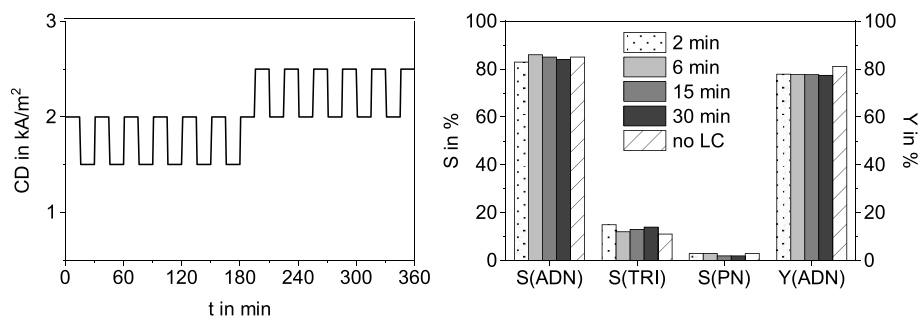


Figure 12. (left) Example of an operation profile with load changes of 25% for 15 min periods. (right) Selectivity toward ADN, the trimerization product (TRI), and PN and yield of ADN with a change of current density by 0.5 kA m^{-2} over varying time periods.

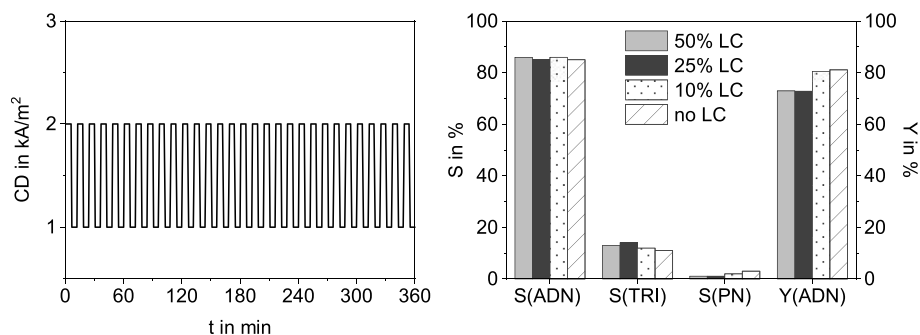


Figure 13. (left) Example of an operation profile with a load decrease of 50% for 6 min periods. (right) Selectivity toward ADN, the trimerization product (TRI), and PN and yield of ADN with varying load changes for 6 min periods compared with a constantly applied current density of 2 kA m^{-2} .

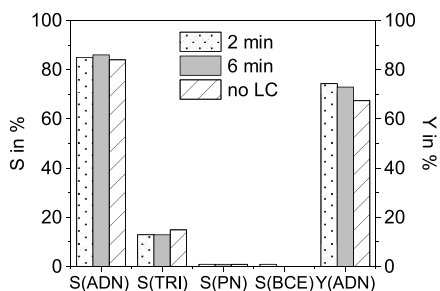


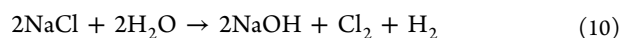
Figure 14. Selectivity toward ADN, the trimerization product (TRI), and PN and yield of ADN for load changing profiles with an average current density of 1.5 kA m^{-2} compared to a constantly applied current density of 1.5 kA m^{-2} after a 6 h reaction time.

ments, similar to the observations in the literature for divided cells.⁹⁴

In summary, the present reaction setup for the electrohydrodimerization of ACN 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 aging 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 LCCs can be estimated. Given the global production volume of 2.1 Mt, adiponitrile has a theoretical global potential for DR of 582 MW, most of which is in China.

4.3. Case Study 3: CAE and Synthesis of 1,2-Dichloroethane. The third case study analyzes the CAE in which hydrogen (H_2), chlorine (Cl_2), and sodium hydroxide (NaOH) are produced. The latter two are commodity chemicals and among the 10 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 Klauke 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 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 Klauke 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 FS of a combined CAE/DCE plant with a nominal power of 100 MW and an installed power of 105 MW (Figure 15), that is, there is an overcapacity of 5%. In the CAE cells, electric power is used to convert aqueous sodium chloride ($\text{NaCl}_{(\text{aq})}$) to sodium hydroxide ($\text{NaOH}_{(\text{aq})}$), chlorine (Cl_2), and hydrogen (H_2):



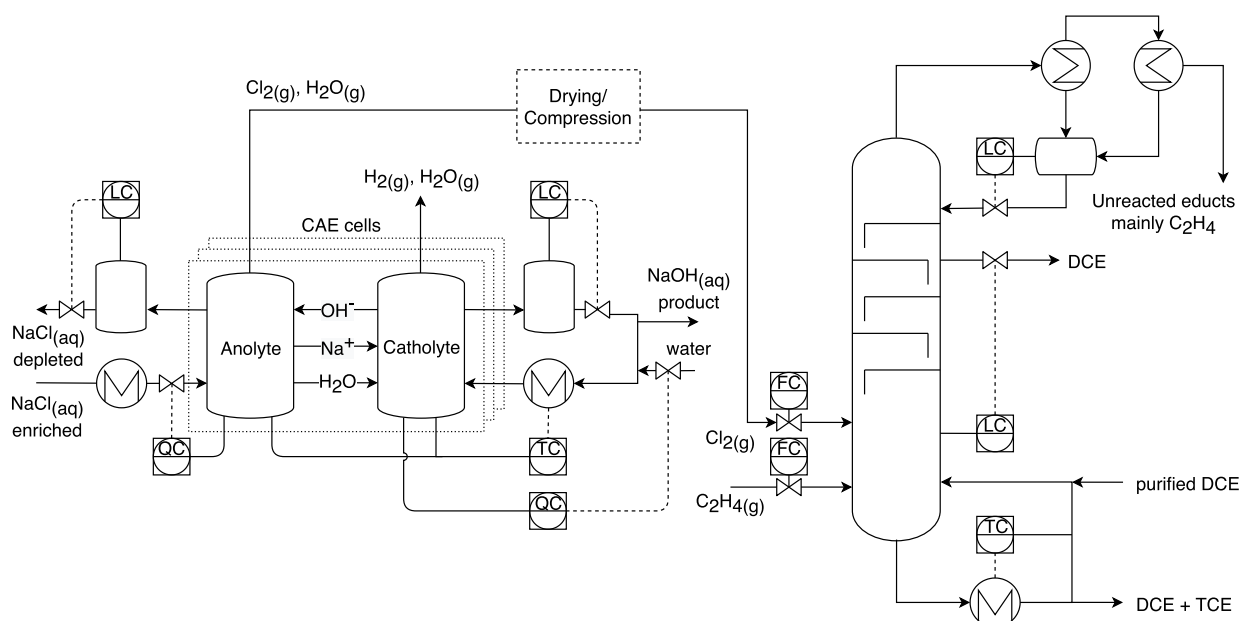


Figure 15. P&I diagram of CAE and DCE production.

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



This reactor serves simultaneously as a 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 byproduct 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 FS 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 FS 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 process³⁴ 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 appears 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, that is, an even smaller value. Nevertheless, DCE storage is strongly preferred as a storage medium over chlorine in practice 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 are 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 categorization 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 kA m^{-2}), which causes the product quality to leave the tolerable range. This value is even more restrictive than the 3 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 analyzed. At high loads, the CAE is limited by a current density of 6 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 a load decrease and 2 for a 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 $P_{\max} = 1.05 P_0$ and $P_{\min} = 0.75 P_0$. 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 BSs, 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 maximum storage capacity of $S_{\max} = 200 t_{\text{DCE}}$ for the storage capacity, which corresponds to 156.4 m³ 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 optimization was also carried out with

Table 5. Optimization Results of the Operation Scheduling Model Developed in Hofmann et al.¹⁹

year	2018		2019	
	c_{LCC} in €/cycle		c_{LCC} in €/cycle	
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 in %	1.32	1.18	1.17	1.01
	3.39	3.03	3.54	3.06
C_{LCC} in € million	--	0.18	--	0.16

specific LCC of € 0 per cycle to analyze their impact on the load profile; that is, 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 LCCs of $c_{\text{LCC}} = € 0$ per cycle, denoted as LCC0, and $c_{\text{LCC}} = € 5000$ 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 LCC, 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 0 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 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 Realizable Potential of DCE Synthesis.

Given the complexity of the dynamic process models and the increased computation times required to solve the respective dynamic optimization problems, such models are not suitable to determine optimal operating policies over a longer time horizon, for example, a year. On the other hand, simplified models are

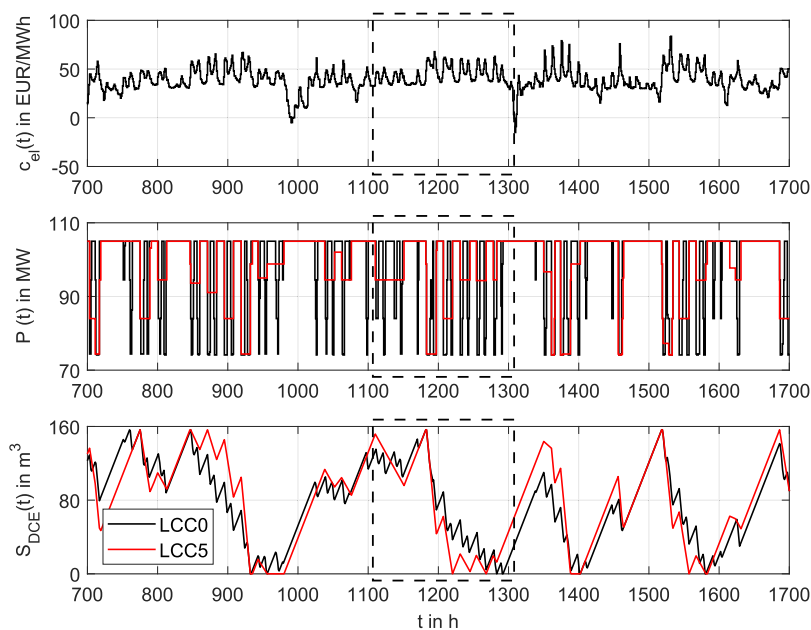


Figure 16. Results of operation scheduling for the power consumption $P(t)$ and the stored amount of DCE $S_{\text{DCE}}(t)$ for different LCCs; $c_{\text{LCC}} = € 0$ per cycle (LCC0) and $c_{\text{LCC}} = € 5000$ per cycle (LCC5) in 2018 (exemplary section). The dashed squares mark the time horizon of the dynamic optimization in the next section.

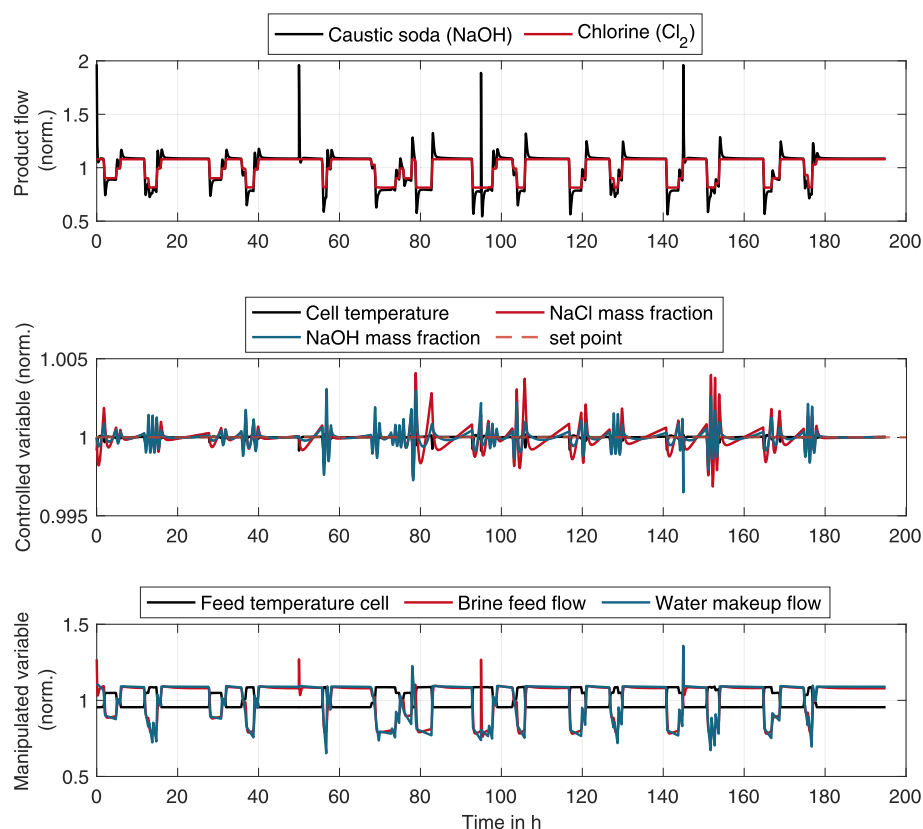


Figure 17. Results of dynamic optimization for CAE to assess the practical potential. Top: product flows of chlorine and caustic soda, normalized using their respective value at nominal load. Mid: control variables of optimal control, normalized based on the corresponding set point. Bottom: manipulated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

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 optimization (marked by dashed boxes in Figure 16) to determine whether the trajectories obtained in the previous section can be realized in a real plant. This time period was chosen because it contained strongly varying loads. We only show results for the case with zero LCC and assume that the less dynamic case with LCC greater than 0 will then also be feasible. Note that extended time periods with low or high load are automatically feasible 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 CAE were suggested by Wang et al.,¹⁰³ Budiarto et al.,¹⁰⁴ and Otashu and Baldea,¹⁷ we use our own dynamic models for CAE¹⁰¹ and DCE production¹⁰⁰ as they have been validated with real process data applicable to the here investigated process concept. Both models are briefly summarized in the following paragraphs.

The CAE model describes the 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 optimization problem given in eq 7a. 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 min is demanded at every set point change.

The CAE part is optimized 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 optimized in a Python/AMPL framework for which time is fully discretized via orthogonal collocation on finite elements.¹⁰⁷ This dynamic

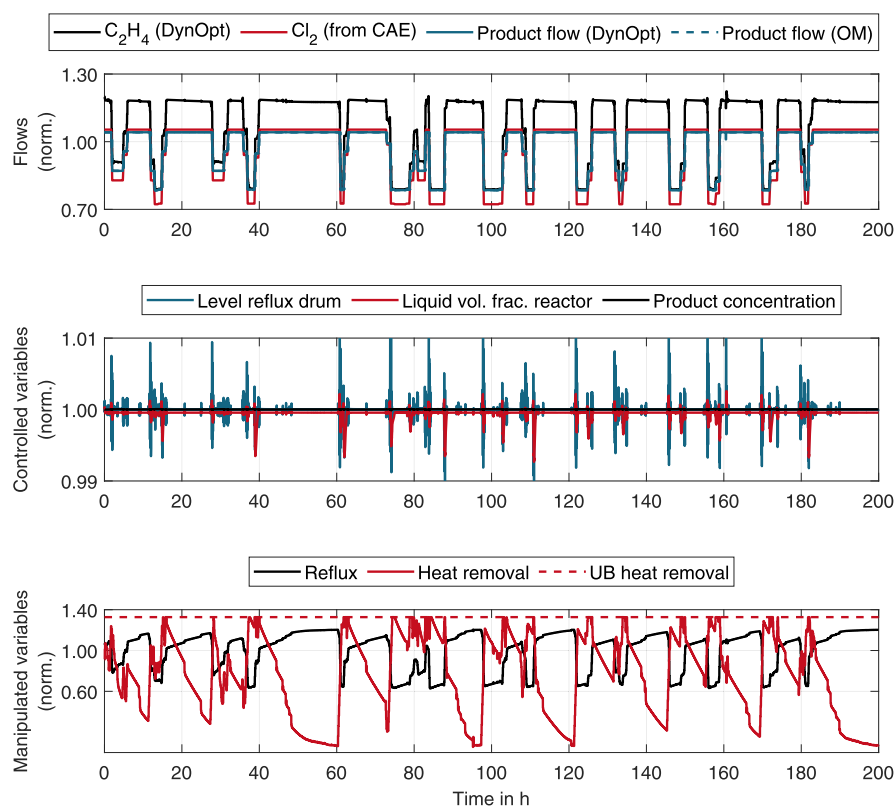


Figure 18. Results of dynamic optimization for DCE production to assess the practical potential. Profiles obtained by dynamic optimization are marked with DynOpt, while trajectories determined with the operation model are marked OM. Top: feed and product flows. Mid: controlled process variables. Bottom: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

optimization 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 one.

Figures 17 and 18 show the results under the DR scenario developed in the previous section. As the models are based on industrial production plants, the data are normalized using their nominal set points; that is, 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 a feed stream for the DCE production. The cell temperature and both the 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 maximum change rate of 1 K min^{-1} and $15 \text{ nom. \% min}^{-1}$.

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 OM, 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, 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 the product concentration, 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 optimization 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 € million per year, depending on the actual year and whether LCC are considered. Note that there is no generic potential for DR 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 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 realizable potential for DR. For this purpose, recent research on the CAE was analyzed 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 optimization. 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 and additional income due to BSs. Occasionally, investment costs for increased plant or storage capacity are considered. However, the additional LCC 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 LCC 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 the 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 backward.

The few studies with rigorous models have so far integrated the economic and practical analyses. According to our methodology, these two potentials are independently determined as 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 realizable 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, for example, 10 MW for mFRR and 1 MW for FCR. Here, more systematic methods to determine the individual load ranges would be desirable. Second, the solution of the scheduling process is still deterministic—the electricity price is known a priori for the whole time horizon and the optimization algorithm may balance operation in an unrealistic way. To address this issue, we propose to solve the scheduling problem with a moving-horizon approach and under uncertainty. This will decrease the problem size and computational effort, respectively, significantly and at the same time yield more realistic results. Last, FCR may not yet be considered in the dynamic optimization 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 optimization problem to determine trajectories that are feasible under such highly frequent fluctuations.

5. CONCLUSIONS AND OUTLOOK

This contribution proposed a methodology to assess the realizable flexibility potential of (electro-)chemical processes for DR applications. The first decision variable in this methodology is the TRL 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, for example, 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 FS must be analyzed to determine the operating window in an FS 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 FS analysis results in a flexibility categorization between A and D and a categorization of load range between 1 and 3. Highly desirable are processes in category A1; that is, their FS revealed negligible barriers for flexible operation and they offer a large

load range. Afterward, a simplified model for operation scheduling is set up to determine the economic potential based on the possible business options by solving an optimization problem, which yields realistic load profiles and product flows. Should a relevant economic potential be determined, dynamic optimization based on rigorous dynamic process models is used to determine whether the trajectories obtained in the previous step are feasible. This yields the realizable 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 H₂O₂ in acid media, which has a TRL below 6. The case study was chosen to illustrate that conventional processes can potentially be replaced with electrochemical processes, which are then able to participate in flexibility markets. We showed that the addition of small amounts of K₂SO₄ significantly enhances the efficiency of this process. While the Faraday efficiency in 0.1 M H₂SO₄ is appreciably lower than that in 0.1 M KOH, the addition of 0.05 M K₂SO₄ decreases the further reduction of H₂O₂ to H₂O 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 stabilizing 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 engineers, and energy engineers to reduce potential bottlenecks for flexible operation right at the beginning.

In Case Study 2, the electrochemical hydrodimerization of ACN 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 LCC.

Finally, Case Study 3 presented the results for the CAE in combination with the synthesis of 1,2-dichloroethane. Following the methodology, we initially determined the operating range using an FS analysis. Then, an economic optimization was carried out, in which electricity was purchased at the day-ahead market. The solution of this optimization problem yielded economic trajectories, which were then applied on validated dynamic process models to determine feasible control profiles via dynamic optimization. Importantly, the optimization problem also considered bounds for control changes. The results showed the process to have a realizable 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 optimization problem.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.1c01360>.

Operating conditions of Case Study 1; operating conditions of Case Study 2; results of the FS analysis of Case Study 3; weighting factors and control constraints for Case Study 3; and comparison of various publications regarding the considered costs as well as control and ramp constraints for Case Study 3 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Christian Hoffmann – *Process Dynamics and Operations Group, Technische Universität Berlin, 10623 Berlin, Germany*; orcid.org/0000-0002-6709-9987; Email: c.hoffmann@tu-berlin.de

Authors

Jessica Hübner – *Department of Chemistry, Technische Universität Berlin, 10623 Berlin, Germany*

Franziska Klauke – *Chair of Energy Engineering and Environmental Protection, Technische Universität Berlin, 10587 Berlin, Germany*

Nataša Milojević – *Department of Chemistry, Technische Universität Berlin, 10623 Berlin, Germany*

Robert Müller – *Chair of Energy Engineering and Environmental Protection, Technische Universität Berlin, 10587 Berlin, Germany*

Maximilian Neumann – *Department of Chemistry, Technische Universität Berlin, 10623 Berlin, Germany*

Joris Weigert – *Process Dynamics and Operations Group, Technische Universität Berlin, 10623 Berlin, Germany*

Erik Esche – *Process Dynamics and Operations Group, Technische Universität Berlin, 10623 Berlin, Germany*

Mathias Hofmann – *Chair of Energy Engineering and Environmental Protection, Technische Universität Berlin, 10587 Berlin, Germany*; orcid.org/0000-0002-1541-3874

Jens-Uwe Repke – *Process Dynamics and Operations Group, Technische Universität Berlin, 10623 Berlin, Germany*

Reinhard Schomäcker – *Department of Chemistry, Technische Universität Berlin, 10623 Berlin, Germany*; orcid.org/0000-0003-3106-3904

Peter Strasser – *Department of Chemistry, Technische Universität Berlin, 10623 Berlin, Germany*; orcid.org/0000-0002-3884-436X

George Tsatsaronis – *Chair of Energy Engineering and Environmental Protection, Technische Universität Berlin, 10587 Berlin, Germany*

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.iecr.1c01360>

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NOMENCLATURE

Abbreviations

2eORR	two-electron oxygen reduction reaction
ACN	acrylonitrile
ADN	adiponitrile
aFRR	automatic frequency restoration reserve
AO	anthraquinone oxidation
BCE	biscyanoethyl ether
BS	balancing service
CAE	chloralkali electrolysis
DCE	1,2-dichloroethane
DR	demand response
DSM	demand-side management
DynOpt	dynamic optimization
FCR	frequency containment reserve
FS	flow sheet
GDL	gas diffusion layer
LCC	cost 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
P&ID	pipe and instrumentation diagram
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
ν	stoichiometric coefficient
ϕ	weighting factor

Latin Symbols

A_{Geo}	area of the electrode, m^2
C	costs, € or € a^{-1}
CD	current density, A m^{-2}
F	Faraday constant, $96,485.3 \text{ A s mol}^{-1}$
FE	Faraday efficiency, %
P	load (power), W
Q	total charge of the system, C
S	storage capacity, kg
S_p	selectivity toward the product, %
V	volume, L
\dot{V}	volume flow, L h^{-1}
Y_p	yield of the product, %
W	work, J
c	molar concentration, mol L^{-1}
c_{el}	Electricity costs, € MWh^{-1}
f	objective function
g	process model
h	path constraints
n	mole amount, mol
r	production rate, $\text{mol m}^{-2} \text{ s}^{-1}$
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}_{max}	restriction for the slope of control change
v_p	rate of load change, W s^{-1}
x	state variables
z	number of transferred electrons

Indices

ce control element

Subscripts

0	nominal operating point
0	at inlet
addInv	additional investment
BS	balancing service
E	educt
LB	lower bound
LCC	costs of load change
P	product
UB	upper bound
down	load decrease
el	electrical
max	maximum
min	minimum
neg	negative
prod	product
pos	positive
up	load increase
var	variable

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