Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Modeling alkaline water electrolysis for power-to-x applications: A scheduling approach

Christopher Varela ^{a,b,*}, Mahmoud Mostafa ^{a,b}, Edwin Zondervan ^b

^a University of Bremen, Faculty of Production Engineering, Leobener Str. 6, Bremen, 28359, Germany

^b University of Twente, Faculty of Science and Technology, Enschede, 7522NB, The Netherlands

HIGHLIGHTS

- A novel scheduling model for alkaline water electrolysis (AEL) has been developed.
- The model introduces AEL states, transitions, and operational characteristics.
- The model allows to find optimal number of electrolyzers and production schedules.
- The model is suitable to handle large data sets of fluctuating energy and prices.
- The MILP solution provides a balance between production, energy absorption and costs.

ARTICLE INFO

Article history:

Received 9 November 2020

Received in revised form

15 December 2020

Accepted 16 December 2020

Available online xxx

Keywords:

Hydrogen

Alkaline water electrolysis

Power-to-x

Mathematical programming

Renewable energy sources

ABSTRACT

The flexible operation of alkaline water electrolyzers enables power-to-x plants to react efficiently to different energy scenarios. In this work, a novel scheduling model for alkaline water electrolysis is formulated as a mixed-integer linear program. The model is constructed by implementing operational states (production, standby, idle) and transitions (cold/full startup, shutdown) as integer variables, while the power loading and hydrogen flowrate are set as continuous variables. The operational characteristics (load range, startup time, ramp rates) are included as model constraints. The proposed model allows finding optimal number of electrolyzers and production schedules when dealing with large data sets of intermittent energy and electricity price. The optimal solution of the case study shows a balance between hydrogen production, energy absorption, and operation and investment costs. The optimal number of electrolyzers to be installed corresponds to 54% of the ones required to absorb the highest energy peak, being capable of loading 89.7% of the available energy during the year of operation, with an overall plant utilization of 93.7% and 764 startup/shutdown cycles evenly distributed among the units.

© 2020 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Recent global environmental commitments, such as the Paris Agreement (COP 21), have led to an increased share of renewable energy sources (RES) in electricity grids. The RES

mix in Germany, consisting of biomass, hydropower, solar- and wind energy, constitutes more than 50% of the net electricity generation [1], with wind energy having the largest share. For wind energy as a non-dispatchable source, the balance of the grid is based on its curtailment during periods

* Corresponding author. University of Bremen, Faculty of Production Engineering, Leobener Str. 6, Bremen, 28359, Germany.

E-mail address: varela@uni-bremen.de (C. Varela).

<https://doi.org/10.1016/j.ijhydene.2020.12.111>

0360-3199/© 2020 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

with excess production, resulting in green energy losses that rose to around 4700 GWh during 2015 in Germany [2]. With high penetrations of wind energy, it becomes essential to provide energy storage systems to the electricity grids, such as thermal (liquid air, latent heat), mechanical (pumped hydro, compressed air), electrical (capacitors, superconducting coils), or electrochemical (batteries, power-to-x) [3].

Power-to-x, defined as the conversion of renewable electricity into chemicals that would otherwise be produced from fossil sources [4], has gained attention over the past few years as a means of decarbonization and integration of sectors such as industry and transportation while improving the stability of grids [3–7]. There are several projects aiming to determine the feasibility of power-to-x at different scales, especially for power-to-gas concepts [8,9]. Further studies highlight the need for operational strategies e.g. demand-side management (DSM), to address the dynamics inherent in energy markets and promote participation in grid services [3,4,10–14]. This drives to consider at the early-stage process design several scenarios for the operation of power-to-x plants according to the seasonal behavior of RES and potential interactions with electricity grids.

The present contribution aims to quantitatively determine the implications on the design and operation of power-to-x plants due to dynamic energy scenarios: renewable energy profile (e.g. Fig. 1) and variable electricity price (e.g. Fig. 2). Since water electrolysis is often the initial step in power-to-x, the study considers the flexible operation of electrolyzers, and their technical limitations, as a framework for applications to methane, methanol, ammonia, and liquid fuels. Finding optimal designs and/or operational strategies becomes a challenging task considering the state-of-the-art non-linear models of water electrolysis and the large data sets on available energy and price. Thus, focus is on developing a mathematical model at production (planning & scheduling) level that computes the energy absorption, hydrogen production, and investment and operation costs, while considering the structure of the energy data: intervals of 1 h during one year of operation i.e. 8760 data points. The proposed scheduling model constitutes a decision-making tool that can be used in practice to determine the number of electrolyzers to be installed and the production schedule that fulfills the process goals for given energy scenarios, allowing to efficiently store renewable energy into hydrogen.

Alkaline water electrolysis: modeling and relevant characteristics for power-to-x applications

Among the electrochemical technologies for hydrogen production, alkaline water electrolysis (AEL) is the most mature with a technology readiness level of TRL-9, compared to proton-exchange membrane electrolysis (PEM) with TRL-8, or high-temperature electrolysis (SOEC) with TRL-5 [17]. AEL technologies are available for large-scale applications, using non-expensive materials for the electrodes such as iron and nickel, while PEM requires iridium and platinum-based catalysts [3]. Due to these factors AEL is the dominant technology in the water electrolysis market nowadays and a viable technology for power-to-x plants.

The most relevant operational features of AEL are listed in Table 1, although some specifications vary widely among manufacturers. Other design specifications of electrolyzers at commercial scale such as electrode active area, number of cells per stack, or electrolyte volumetric flowrate, are not available in the public domain. Ancillary equipment for heat- and flow management (compressors, pumps, gas-liquid separators, purification units) allow keeping the process variables quasi-constant during the operation. In addition, transformers and rectifiers are used to convert high voltage alternating current from the grid to direct current [3,18–20].

Modeling AEL has become a major field of research due to the increasing penetration of RES in electricity grids and the efforts to find alternatives to fossil fuels. Although electrolyzers have been commercialized and used by industry for decades, reaching the highest TRL, the multiphase and multiscale phenomena that rules their operation are still under investigation [20,24–26]. The zero-dimensional model developed by Haug et al. [27] is based on material balances of lumped compartments, introducing correlations for mass transfer between the gas- and liquid (electrolyte) phase, as well as the transport between the anode- and cathode side of a lab-scale electrolysis cell, which allows to determine the composition of the gas products as a function of the operating conditions. The model proposed by Ulleberg [28] has been widely used by many authors as it requires a low number of experimental parameters to construct the polarization curve that characterizes the operation of electrolyzers, allowing to perform estimations for large scale applications.

Fig. 1 – 50-MW wind energy, Heide (Germany) 2019. Simulated from the model of Pfenniger and Staffell [15].

Fig. 2 – Day-ahead energy price, Germany 2019. Data extracted from Bundesnetzagentur SMARD [16].

Table 1 – AEL specifications [3,19,21–23].

Electrolyte	20–40% KOH (w/w)
Current density	0.2–0.45 A/cm ²
Voltage per cell	1.8–2.4 V
Temperature	50–80 °C
Pressure	1–30 bar
Capacity	1–450 Nm ³ /h
Durability	1E5 h
Operation range	15–100% nominal
Stack consumption	4.2–5.9 kWh/Nm ³
System consumption	4.5–7.0 kWh/Nm ³
H ₂ purity	99.8–99.9% (V/V)
O ₂ purity	99.3–99.8% (V/V)

The integration of AEL models with energy systems has been investigated by many authors in terms of frequency control strategies [11,29,30], techno-economic assessments [13,31–33], and experimental setups [34–36]. The work from Matute et al. [37] introduces operational states of an electrolysis plant (production, standby and idle) to determine the optimal dispatch of hydrogen under dynamic operation.

The novelty in the present work lies on the mathematical description of the operational states, their transitions, and main operational characteristics of AEL, to compute the energy absorption, production of hydrogen, and costs at production level. This approach allows using the degrees of freedom of electrolyzers to determine the most suitable operation when dealing with fluctuating energy and price profiles. Since AEL is suitable when dealing with energy fluctuations by adjusting the loading of electrolyzers or moving the operation towards standby or idle states, models that fully describe its operation at different operational states, their transitions, and limitations are required. The model is limited however to calculations at production level, considering an input-output behavior of the stacks while the phenomena within the electrolysis cells are not directly computed.

While the operational states of AEL are production, standby and idle, the transitions between states correspond to cold/full startup and shutdown cycles. The main operational characteristics of AEL to consider when dealing with intermittent renewable energy are load range, ramp up- and down rate, and startup and shutdown time [19,38].

- **Load range:** Electrolyzers can operate between 15 and 100% of their nominal capacity [3,22,39,40]. However, these operation limits cannot be violated as a measure of avoiding risk scenarios, namely explosive gas mixtures at lower current densities, and damage to stack materials at higher current densities than the nominal [19]. New technologies allow minimum loads of 10% [40], however in this work the minimum load of 15% of the nominal capacity is selected according to most specifications of manufacturers. The load limits constitute hard constraints to the model proposed in this work to prohibit risk scenarios.
- **Ramp up- and down rate:** The response time to load changes depends on an adequate installation of power electronics and correct handling of the gas flow within the electrolyzer [38]. New developments on alkaline water electrolyzers permit ramp up- and down rates in the range of few seconds [41]. Ramp rates (up and down) of 20% of the nominal load per second is conventionally accepted [42].
- **Startup and shutdown time:** It is reported a duration of 30–60 min to restart the unit operation as the complete system (stack, cooling, purification and compression units) must be purged [43]. The restart of the operation after standby mode (cold startup) requires approximately 20 min [42].

This work is divided into three main sections: Methodology, that contains the modeling approach and variables definition; Model development, where the mixed-integer linear program is shown with a detailed explanation of the objective function and model constraints; and Model application, in which the model is used to determine the optimal design and production schedule of plant that uses solely wind energy to produce renewable hydrogen.

Methodology

The proposed scheduling model is formulated as a mixed-integer linear program (MILP). The approach resembles to the one used for the Unit Commitment Problem [44], with the distinction that the energy is stored in the form of hydrogen rather than produced to satisfy energy demands, and the units are identical electrolyzers instead of power generators.

The following integer (binary) variables are introduced to describe the operational states of alkaline water electrolyzers:

- Production state “L”
- Standby state “S”
- Idle state “I”

Two additional binary variables are included to compute the startup and shutdown cycles:

- Startup cycle “Y”
- Shutdown cycle “Z”

Finally, the continuous variables that characterize the input-output behavior of electrolyzers are:

- Power load “U”
- Hydrogen flowrate “F”

A graphic description of the proposed model for alkaline water electrolysis is presented in Fig. 3, with the variables and allowed values at each operational state and transition.

During the time interval “t”, the electrolyzer “n” at idle state “I” is not allowed to load ($U = 0$) and, therefore, produces no hydrogen ($F = 0$); while at standby state “S”, it requires a standby loading ($U = U^{SB}$), but the production of hydrogen is zero. At production state “L” the load can be decided according to the load range (U^{MIN} , U^{MAX}) and the production of hydrogen is a function of the selected load. The transitions between the states (arrows) allow to include:

- full startup time ($I \rightarrow S$ or $I \rightarrow L$) as a penalty on the electrolyzer availability,
- cold startup ($S \rightarrow L$) as a penalty on the electrolyzer production rate, and
- costs for startup and shutdown cycles.

Fig. 3 – Timed automaton representation of alkaline water electrolyzers.

This novel approach increases the degrees of freedom of the alkaline water electrolysis model as compared to previous models that only consider the production state “L” or neglect the transitions, resulting in a more detailed description of the operation under non-steady conditions.

Model development

Given profiles of energy availability and electricity price as model parameters (Figs. 1 and 2), the optimal operation schedule of the electrolysis plant can be determined by formulating the mixed-integer program represented in Problem 1.

$$\max_{x_{n,t}} \text{Obj} \quad (\text{Problem 1})$$

subject to:

$$\begin{aligned} A_t^L &\leq h(x_{n,t}) \leq A_t^U \\ x_{n,t} &= [U_{n,t}, F_{n,t}, L_{n,t}, S_{n,t}, I_{n,t}, Y_{n,t}, Z_{n,t}] \\ U_{n,t}, F_{n,t} &\in \{0, \mathbb{R}^+\} \\ L_{n,t}, S_{n,t}, I_{n,t}, Y_{n,t}, Z_{n,t} &\in \{0, 1\} \\ n &= \{1, \dots, N\} \\ t &= \{t_0, \dots, t_f\} \end{aligned}$$

Objective function

The process goal is to efficiently convert renewable energy into hydrogen. The production rate “ $F_{n,t}$ ”, which is a function of the electrolyzer load “ $U_{n,t}$ ” and operational state (Fig. 3), can change according to the energy scenario: high energy availability, low energy availability, high electricity price, and low electricity price.

$$\begin{aligned} \text{Obj} = & K \sum_{t=t_0}^{t_f} \sum_{n=1}^N F_{n,t} - \sum_{t=t_0}^{t_f} C_t^{WP} \sum_{n=1}^N U_{n,t} - \sum_{t=t_0}^{t_f} \sum_{n=1}^N (Y_{n,t} C^{SU} + Z_{n,t} C^{SD}) \\ & - N \frac{C^{INV}}{LT} \end{aligned} \quad (1)$$

The terms from Eq. (1) correspond to (1) the income for the total production of hydrogen; (2) the total electricity cost for the operation of the electrolyzers with variable electricity price; (3) the total cost for startup and shutdown; and, (4) the investment cost for the installation of “N” electrolyzers over their lifetime. In such way, the objective is to balance the energy absorption with the annual production of hydrogen, and operation and investment costs.

Decision variables

The scheduling model includes as continuous variables the energy load “ $U_{n,t}$ ” and hydrogen flowrate “ $F_{n,t}$ ”, and as binary variables the operational states: production “ $L_{n,t}$ ”, standby “ $S_{n,t}$ ” and idle “ $I_{n,t}$ ”, and counters for startup “ $Y_{n,t}$ ” and shutdown cycles “ $Z_{n,t}$ ”, for each electrolyzer “n” at time interval “t”, as shown in Fig. 3.

Constraints

The model constraints correspond to the mathematical description of the operation of electrolyzers that includes in the form of heuristic rules the operational characteristics of electrolyzers and physical constraints of the system.

System capacity constraint

The total energy load is limited to the available energy source. For the case study, the energy source “ U_t^{WP} ” corresponds to the wind power data shown in Fig. 1.

$$\sum_{n=1}^N U_{n,t} \leq U_t^{WP} \quad (2)$$

$$\forall t \in \{t_0, \dots, t_f\}$$

Electrolyzer capacity (safety) constraint

The load is bounded to the load range (U^{MIN} , U^{MAX}). The proposed formulation allows including energy requirements at standby state (U^{SB}), and no energy consumption at idle state.

$$U^{SB} S_{n,t} + L_{n,t} U^{MIN} \leq U_{n,t} \leq U^{SB} S_{n,t} + L_{n,t} U^{MAX} \quad (3)$$

$$\forall t \in \{t_0, \dots, t_f\}, \quad \forall n \in \{1, \dots, N\}$$

Electrolyzer production constraint

An input-output correlation for the production rate of hydrogen “ $F_{n,t}$ ” as a function of the electrolyzer load “ $U_{n,t}$ ” is constructed in this study based on the current-voltage model proposed by Ulleberg [28]:

$$V_{el} = N_{cells} \left[V_{rev} + \frac{r_1 + r_2 T}{A_{el}} I + s \log \left(\frac{t_1 + \frac{t_2}{T} + \frac{t_3}{T^2}}{A_{el}} I + 1 \right) \right] \quad (4)$$

The production of hydrogen as a function of the energy load provides an operational window that sets the limits of production rate and load range. The performance of a commercial alkaline electrolyzer is shown in Fig. 4, considering an electrode effective area of 2.7 m², 80 cells, and energy requirements of 4.67 kWh/Nm³ for the rated load [45], considering the same parameters provided in the work of Ulleberg [28]. The maximum load correspond to theoretical load with

Fig. 4 – Production of hydrogen as a function of the energy load.

current densities of 0.45 A/cm² [3]. Fig. 4 includes first and second order approximations to construct the input-output correlation.

The second order approximation matches the operation at 80 °C and 1 bar, including the maximum and minimum load, while the linear approximation includes the minimum and rated load as interpolators. The expressions for the first and second order approximations are shown in Eqs. (5) and (6), with hydrogen flowrate in Nm³/h and power load in MW, and their validity range between the maximum and minimum load, and T-P conditions.

$$F = 205.31 U + 17.85 \quad (5)$$

$$F = -11.24 U^2 + 232.7 U + 8.89 \quad (6)$$

With a minimum yet non-negligible deviation (Root Mean Squared Error of 5.49), the linear approximation is preferred at the time of computing large data sets, especially for optimization as many iterations are required. Therefore, Eq. (5) is used as input-output (load-flowrate) correlation, while Eq. (6) can be used for more accurate flowrate estimations in models of smaller size.

The resulting input-output correlation is combined with the binary variables of the program to compute the production of hydrogen at each state. A linearized function is presented in Eqs. (7)–(10), with the introduction of the slack binary variable “ $W_{n,t}$ ” that represents transitions from standby to production state in consecutive intervals of time ($S_{n,t-1} \rightarrow L_{n,t}$).

$$F_{n,t} = A_1 (U_{n,t} - S_{n,t} U^{SB}) + A_2 L_{n,t} - A_3 W_{n,t} \quad (7)$$

$$W_{n,t} \leq S_{n,t-1} \quad (8)$$

$$W_{n,t} \leq L_{n,t} \quad (9)$$

$$W_{n,t} \geq S_{n,t-1} + L_{n,t} - 1 \quad (10)$$

$$\forall t \in \{t_1, \dots, t_f\}, \quad \forall n \in \{1, \dots, N\}$$

The coefficients A_1 and A_2 are obtained from the construction of the input-output correlation, which are specific to the electrolyzer design. The coefficient A_3 corresponds to a penalty on the production rate of one-third when the slack variable “ $W_{n,t}$ ” is active, as the time required for cold startups is 20 min and the time intervals of the scheduling program are fixed to 1 h. It can be noticed that for states different than the production state i.e. $L_{n,t} \neq 1$, the flowrate of hydrogen goes to zero.

Ramp up- and down rate constraint

The ramp rates are restricted according to the following expression:

$$U_{n,t-1} - RD \leq U_{n,t} \leq U_{n,t-1} + RU \quad (11)$$

$$\forall t \in \{t_1, \dots, t_f\}, \quad \forall n \in \{1, \dots, N\}$$

Logic constraints for transitions between states

The time required to restart the operation after shutdown (idle) periods is 1 h. With intervals of 1 h this can be interpreted as a penalty on the unit availability of one interval of

time, considering previous and current values of the state variable “T”.

$$-I_{n,t-2} + I_{n,t-1} - I_{n,t} \leq 0 \quad (12)$$

$$\forall t \in \{t_2, \dots, t_f\}, \quad \forall n \in \{1, \dots, N\}$$

The integer variables to compute cycles of startup “ $Y_{n,t}$ ” and shutdown “ $Z_{n,t}$ ” follow the rules shown in Eqs. (13) and (14).

$$L_{n,t} + S_{n,t} + I_{n,t-1} - 1 \leq Y_{n,t} \quad (13)$$

$$L_{n,t-1} + S_{n,t-1} + I_{n,t} - 1 \leq Z_{n,t} \quad (14)$$

$$\forall t \in \{t_1, \dots, t_f\}, \quad \forall n \in \{1, \dots, N\}$$

Lastly, the scenario for simultaneous production, standby and idle state is prohibited by including the following logic expression:

$$L_{n,t} + S_{n,t} + I_{n,t} = 1 \quad (15)$$

$$\forall t \in \{t_0, \dots, t_f\}, \quad \forall n \in \{1, \dots, N\}$$

Problem structure and size

The proposed formulation leads to a mixed-integer linear program (MILP), where the number of electrolyzers and number of time intervals significantly influence the size of the program. Considering lower intervals than 1 h would allow to compute fast changes in the operation, for instance, primary control reserve and temperature changes, however the current model setup permits to find optimal number of stacks and production schedules over large time horizons with moderate computational effort. For the case study of 50-MW hydrogen plant, a variable number of electrolyzers “N” is used as a strategy to find the optimal number of electrolyzers while keeping the linearity of the optimization problem. On the other hand, the number of time intervals is set to 8760, for intervals of 1 h over a year. With 25 installed electrolyzers, the MILP contains 438000 binary variables, 876000 continuous variables and 2198710 equations.

Model application. Case study: 50-MW renewable hydrogen plant (power-to-x)

The scheduling model is implemented to find the optimal production schedule of a hydrogen plant powered with 50 MW

(nominal) of wind energy in Northern Germany. The model parameters are shown in Table 2.

The startup and shutdown costs (C^{SU} and C^{SD}) are conservatively estimated due to the lack of information in the public domain on this regard. The startup cost is calculated based on the maximum load with a constant electricity price of 50 EUR/MWh for one interval, while the shutdown cost is zero in terms of electricity consumption. However, it is expected that the implemented penalty on the availability of the units (Eq. (12)), production loss (Eq. (7)) and additional costs for switching between operational modes (Eqs. (13) and (14)) have a major incidence at the time of finding optimal schedules. The parameter for standby load is a guess between no load at idle state and the minimum load at production state, with the highest value promoting transitions to standby state rather than shutdown cycles. Also, due to the considerably large values for ramp up- and down rates, and fixed 1-h intervals of time, the ramp up- and down constraint (Eq. (11)) can be neglected.

Solver

The solution is obtained by implementing the scheduling model (MILP) with the parameters for the case study (Table 2) in the optimization platform GUROBI [46]. The solver combines a branch-and-cut algorithm with barrier or simplex method for the continuous problem at the MIP nodes.

Results and discussion

Optimal number of electrolyzers

The most efficient operation is performed with 13 electrolyzers, as shown in Figs. 5 and 6. These figures have been constructed by solving the scheduling program (MILP) with different values of “N”. It is noticed that the more units are installed the higher the investment cost increases, and with a reduction of the number of electrolyzers the installed capacity of wind energy is neither fully nor efficiently used. Therefore, the proper balance between production, energy absorption, and operation and investment costs is obtained by installing 13 electrolyzers.

For the highest energy peak ($U^{WP} = 49.4$ MW, $t = 1506$ h) more than 24 electrolyzers are required. However, the optimal

Table 2 – Model parameters of the case study.

K	0.34 EUR/Nm ³
C_i^{WP}	{28.3,...,37.4} EUR/MWh (Fig. 2)
C^{SU} , C^{SD}	105.1 EUR/h, 0 EUR/h
C^{INV}	$1.47 \cdot 10^6$ EUR
N	{1,...,25} electrolyzers
LT	7.5 a
U_i^{WP}	{40.8,...,10.1} MW (Fig. 1)
U^{SB}	0.30 MW
U^{MIN} , U^{MAX}	0.35 MW, 2.10 MW
A_1 , A_2	205.31 Nm ³ /MWh, 17.85 Nm ³ /h
RD/RU	1512 MW/h

Fig. 5 – Objective value for different number of installed electrolyzers.

Fig. 6 – Correlation between the objective value and total energy absorption.

number of electrolyzer ($N = 13$) allows loading 89.68% of the available renewable energy within the given time horizon, as shown in Figs. 6 and 7. Therefore, with a reduction in the investment cost of 45.83%, it is possible to convert 89.7% of the total energy into hydrogen. In the practice this means that the loading limit of the plant is 27.31 MW, and higher peaks are not to be absorbed due to economic reasons.

Optimal production schedule

The operational states of the 13 electrolyzers are shown in Figs. 8 and 9, whereas their power load is presented in Fig. 10. Although the full-time horizon has been used for optimization purposes, the figures only present a few arbitrarily selected sections over the given time horizon to illustrate the behavior of the electrolysis plant.

The computed utilization of the plant, which is defined as the total intervals in which the units are not in idle state, rises to 91.37%. This means that during most of the time intervals the units are operating despite several periods of low availability of energy. With only 53 standby periods found in the optimal schedule (Fig. 9), the strategy chosen by the MILP-solver consists of an operation within the load ranges i.e. $L = 1$. Although the selection of partial loads rather than standby or shutdown is the expected decision, the low number of standby periods leads to further refinement of the cost parameters for startup and shutdown cycles, or to the implementation of additional constraints. The number of startup/shutdown cycles is 764, yet the implications and restrictions have to be determined by manufacturers and operators. However, the periods at production, standby, and idle state have been uniformly distributed over the electrolyzers

Fig. 7 – System load as cumulative energy absorption with 8, 13, 17 and 20 electrolyzers.

Fig. 8 – Optimal schedule with arbitrarily selected sections.

Fig. 9 – Number of periods (log scale) at production, standby, idle, and startup/shutdown cycles.

(Fig. 9), which indicates that the electrolyzers are required to change between operational states in the same extent to cope with intermittent renewable energy.

The optimization provides the distinct partial load of electrolyzers along the time horizon (Fig. 10), that otherwise would be trivial to determine and would require high computational effort. At production state ($L = 1$) the load is always within the allowed operation range: $U \in [0.35, 2.10]$ MW, while at idle state ($I = 1$) the load is zero e.g. Electrolyzer No. 1 at $t \in [8635, 8636]$ h. At standby state ($S = 1$) the load corresponds to the parameter U^{SB} (0.30 MW) e.g. Electrolyzers No. 9, 10 and 13 at $t = 58$ h. Furthermore, the full startup constraint (Eq. (12)) is fulfilled as none of the electrolyzers switches from idle to production (or standby) state without the penalty of one interval of time.

It is observed that the units are mostly loading at maximum or minimum production capacity, which reflects the operation strategy of keeping the production state of the units while following the energy source fluctuations. The load distribution indicates that 48% of the time intervals the plant performs a maximum load, while 37% its minimum value at production state. The high number of periods at maximum load is due to the system capacity of around 27 MW (13 units with 2.10 MW/unit) while the highest peak of energy is around 50 MW. The low number of periods at minimum load confirms that through optimization it is possible to deal with intervals of low energy availability while keeping most of the units at production state, avoiding penalties on the production rate or availability of electrolyzers.

Fig. 10 – Optimal load of electrolyzers in MW.

Fig. 11 – High-price interval.

The flowrate of hydrogen follows a similar profile presented in Fig. 10, except for the transitions from standby to production state as a penalty has been introduced in the model formulation (Eq. (7)). For instance, at $t = 5419$ h the Electrolyzer No. 5 loads 0.562 MW to produce $103.23 \text{ Nm}^3/\text{h}$ out of possible $133.23 \text{ Nm}^3/\text{h}$, due to the penalty on the flowrate for cold startups. Due to the low number of standby periods, and therefore, few cold startup cycles, this penalty has no major effect.

Plant reaction to variable electricity price

The system response to variable energy prices has been analyzed. In the objective function (Eq. (1)) the energy price appears as a time-variant weight to the total load. Therefore, at high energy prices the system is expected to reduce its load, while low (or negative) prices ought to lead to the decision to increase the production rate of hydrogen by raising the plant load. Consider, for instance, in Fig. 2 the time intervals of $t \in [550, 600]$ h as high-cost period, and $t \in [3780, 3830]$ h as low-cost period. The system responses are shown in Figs. 11 and 12. The optimal solution follows the expected strategy

Fig. 12 – Low-price interval.

of benefiting from low-price intervals, and a conservative operation during high-price intervals.

Conclusions

The proposed scheduling model for alkaline water electrolysis allows determining optimal production schedules for the efficient conversion of renewable energy into hydrogen, considering fluctuations in energy availability and price over large time horizons. The unique features of the scheduling model are the operational states and transitions introduced as decision variables, and operational characteristics implemented as constraints. The electrolysis model allows for production, standby and idle state, cold startups, full startups, and shutdowns. The load range of the units and startup time are rules that allow to compute a realistic operation under non-steady conditions. The correlation between load and hydrogen flowrate developed in this work together with the strategy of solving the scheduling model for several number of stacks, allowed to keep the linearity of the mixed-integer program, and consequently, to find solutions despite the model size. The configuration of the model allows to introduce several energy sources and different cost parameters in the objective function.

The application of the scheduling model in the case study shows a balance between production of hydrogen, energy absorption, and operation and investment costs. Therefore, with a forecast of renewable energy and prices, it is possible to determine the optimal number of stacks to be installed and the optimal production schedule. Such estimations allow to decide on viable options for large-scale applications of power-to-x processes. For many numbers of time intervals and electrolyzers, the optimization allowed to obtain optimal loading profiles in few seconds, complying with the technical restrictions introduced at the model constraints.

With 50 MW of fluctuating wind energy, it is possible to absorb almost 90% of the available energy produced in one year using 13 electrolyzers. Although the plant capacity corresponds to 54% of the nominal wind energy, the low frequency of high peaks of energy makes the installation of more electrolyzers unattractive, giving considerably lower objective values. The optimal production schedule shows the most convenient operation strategy: to operate mainly between the load boundaries i.e. at production state. The overall results indicate a maximum load over 48% of the time intervals, while the minimum load occurs during 37% of the periods. The low number of standby periods (53 periods) as compared to shutdown cycles (764 periods) indicates that the model parameters can be refined with data from manufacturers and operators, especially the operation costs and maximum number of startup and shutdown cycles.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Funding of this research by the German Federal Ministry of Economic Affairs and Energy within the KEROSyN100 project (funding code 03EIV051A) is gratefully acknowledged.

Nomenclature

Variables

F	Hydrogen flowrate (Nm ³ /h)
L	Binary variable for idle mode
P	Pressure (bar)
S	Binary variable for standby mode
T	Temperature (°C)
U	Energy load (MW)
W	Binary slack variable for production penalty
Y	Binary variable for startup cost count
Z	Binary variable for shutdown cost count

Parameters

A _i	Coefficient for input-output correlation
C ^{INV}	Investment cost
C ^{SU, SD}	Startup, shutdown cost
C ^{WP}	Energy price
K	Hydrogen price
n	Index for electrolyzer number
N	Total number of electrolyzers
RD, RU	Ramp up-and down rate
t	Index for time interval
U ^{SB, MIN, MAX}	Standby, minimum, maximum load

REFERENCES

- [1] Fraunhofer Institute for Solar Energy Systems. Net public electricity generation in Germany in 2020. Fraunhofer ISE; 2020 [Online]. Available: https://www.energy-charts.de/energy_pie.htm. [Accessed 23 March 2020].
- [2] Rohrig K (Hrsg). Windenergie report deutschland 2012. 2013.
- [3] Moseley PT, Garche J. Electrochemical energy storage for renewable sources and grid balancing. Elsevier; 2015.
- [4] Burre J, Bongartz D, Brée L, Roh K, Mitsos A, Power-to-X “. Between electricity storage, e-production, and demand side management. Chem Ing Tech Jan. 2020;92(1–2):74–84. <https://doi.org/10.1002/cite.201900102>.
- [5] Götz M, et al. Renewable Power-to-Gas: a technological and economic review. Renew Energy 2016;85:1371–90. <https://doi.org/10.1016/j.renene.2015.07.066>.
- [6] Schmidt P, Batteiger V, Roth A, Weindorf W, Raksha T. Power-to-Liquids as renewable fuel option for aviation: a review. Chem Ing Tech 2018;90(1):127–40. <https://doi.org/10.1002/cite.201700129>.
- [7] S. Energy. 20200710_PtX_White paper_en. 2020.
- [8] Gahleitner G. Hydrogen from renewable electricity: an international review of power-to-gas pilot plants for stationary applications. Int J Hydrogen Energy 2013;38(5):2039–61. <https://doi.org/10.1016/j.ijhydene.2012.12.010>.
- [9] Thema M, Bauer F, Sterner M. Power-to-Gas: electrolysis and methanation status review. Renew Sustain Energy Rev 2019;112(January):775–87. <https://doi.org/10.1016/j.rser.2019.06.030>.
- [10] Seibel C, Kuhlmann JW. Dynamic water electrolysis in cross-sectoral processes. Chem Ing Tech 2018;90(10):1430–6. <https://doi.org/10.1002/cite.201800114>.
- [11] Bolívar Jaramillo L, Weidlich A. Optimal microgrid scheduling with peak load reduction involving an electrolyzer and flexible loads. Appl Energy 2016;169:857–65. <https://doi.org/10.1016/j.apenergy.2016.02.096>.
- [12] Troncoso E, Newborough M. Implementation and control of electrolyzers to achieve high penetrations of renewable power. Int J Hydrogen Energy 2007;32(13):2253–68. <https://doi.org/10.1016/j.ijhydene.2007.02.034>.
- [13] Matute G, Yusta JM, Correás LC. Techno-economic modelling of water electrolyzers in the range of several MW to provide grid services while generating hydrogen for different applications: a case study in Spain applied to mobility with FCEVs. Int J Hydrogen Energy 2019;44(33):17431–42. <https://doi.org/10.1016/j.ijhydene.2019.05.092>.
- [14] Kiaee M, Cruden A, Infield D, Chladek P. Improvement of power system frequency stability using alkaline electrolysis plants. Proc Inst Mech Eng Part A J Power Energy 2013;227(1):115–23. <https://doi.org/10.1177/0957650912466642>.
- [15] Staffell I, Pfenninger S. Using bias-corrected reanalysis to simulate current and future wind power output. Energy 2016;114:1224–39. <https://doi.org/10.1016/j.energy.2016.08.068>.
- [16] Bundesnetzagentur SMARD. Market data visuals. 2020 [Online]. Available: <https://www.smard.de/en/5790>. [Accessed 19 May 2020].
- [17] Schmidt P, Weindorf W. Power-to-Liquids: potentials and perspectives for the future supply of renewable aviation fuel. 2016. p. 1–36. Dessau-Roßlau, no. september.
- [18] Godula-jopek A. Hydrogen science and electrochemical science and technology – fundamentals electrochemical technologies for energy storage and fuel cell science and high energy density lithium. 2015.
- [19] Carmo M, Stolten D. Energy storage using hydrogen produced from excess renewable electricity. Elsevier Inc.; 2019.
- [20] Zeng K, Zhang D. Recent progress in alkaline water electrolysis for hydrogen production and applications. Prog Energy Combust Sci Jun. 2010;36(3):307–26. <https://doi.org/10.1016/j.pecs.2009.11.002>.
- [21] Millet P, Grigoriev S. Water electrolysis technologies. 2013. p. 19–41. <https://doi.org/10.1016/B978-0-444-56352-1.00002-7>.
- [22] Nel, “The World ’ s Most Efficient and Reliable Electrolyzers,” 2019. [Online]. Available: <https://nelhydrogen.com/product/atmospheric-alkaline-electrolyser-a-series/>. [Accessed: 31-Oct-2019].
- [23] Carmo M, Fritz DL, Mergel J, Stolten D. A comprehensive review on PEM water electrolysis. Int J Hydrogen Energy 2013;38(12):4901–34. <https://doi.org/10.1016/j.ijhydene.2013.01.151>.
- [24] Hammoudi M, Henao C, Agbossou K, Dubé Y, Doumbia ML. New multi-physics approach for modelling and design of alkaline electrolyzers. Int J Hydrogen Energy 2012;37(19):13895–913. <https://doi.org/10.1016/j.ijhydene.2012.07.015>.
- [25] Milewski J, Guandalini G, Campanari S. Modeling an alkaline electrolysis cell through reduced-order and loss-estimate approaches. J Power Sources 2014;269:203–11. <https://doi.org/10.1016/j.jpowsour.2014.06.138>.
- [26] Haug P, Koj M, Turek T. Influence of process conditions on gas purity in alkaline water electrolysis. Int J Hydrogen Energy 2017;42(15):9406–18. <https://doi.org/10.1016/j.ijhydene.2016.12.111>.
- [27] Haug P, Kreitz B, Koj M, Turek T. Process modelling of an alkaline water electrolyzer. Int J Hydrogen Energy

- 2017;42(24):15689–707. <https://doi.org/10.1016/j.ijhydene.2017.05.031>.
- [28] Ulleberg Ø. Modeling of advanced alkaline electrolyzers: a system simulation approach. *Int J Hydrogen Energy* 2003;28(1):21–33. [https://doi.org/10.1016/S0360-3199\(02\)00033-2](https://doi.org/10.1016/S0360-3199(02)00033-2).
- [29] Miland H, Glöckner R, Taylor P, Jarle Aaberg R, Hagen G. Load control of a wind-hydrogen stand-alone power system. *Int J Hydrogen Energy* 2006;31(9):1215–35. <https://doi.org/10.1016/j.ijhydene.2005.09.005>.
- [30] Kiaee M, Cruden A, Infield D, Chladek P. Utilisation of alkaline electrolyzers to improve power system frequency stability with a high penetration of wind power. *IET Renew Power Gener* 2014;8(5):529–36. <https://doi.org/10.1049/iet-rpg.2012.0190>.
- [31] Troncoso E, Newborough M. “Electrolysers for mitigating wind curtailment and producing ‘green’ merchant hydrogen. *Int J Hydrogen Energy* 2011;36(1):120–34. <https://doi.org/10.1016/j.ijhydene.2010.10.047>.
- [32] Ochoa Bique A, Maia LKK, La Mantia F, Manca D, Zondervan E. Balancing costs, safety and CO2 emissions in the design of hydrogen supply chains. *Comput Chem Eng* 2019;129. <https://doi.org/10.1016/j.compchemeng.2019.06.018>.
- [33] Schnuelle C, Wassermann T, Fuhrlaender D, Zondervan E. Dynamic hydrogen production from PV & wind direct electricity supply – modeling and techno-economic assessment. *Int J Hydrogen Energy Sep.* 2020. <https://doi.org/10.1016/j.ijhydene.2020.08.044>.
- [34] Dukić A, Firak M. Hydrogen production using alkaline electrolyzer and photovoltaic (PV) module. *Int J Hydrogen Energy* 2011;36(13):7799–806. <https://doi.org/10.1016/j.ijhydene.2011.01.180>.
- [35] Gandía LM, Oroz R, Ursúa A, Sanchis P, Diéguez PM. Renewable hydrogen production: performance of an alkaline water electrolyzer working under emulated wind conditions. *Energy Fuels* 2007;21(3):1699–706. <https://doi.org/10.1021/ef060491u>.
- [36] Ursúa A, San Martín I, Barrios EL, Sanchis P. Stand-alone operation of an alkaline water electrolyser fed by wind and photovoltaic systems. *Int J Hydrogen Energy* 2013;38(35):14952–67. <https://doi.org/10.1016/j.ijhydene.2013.09.085>.
- [37] Matute G, Yusta JM, Beyza J, Correias LC. Multi-state techno-economic model for optimal dispatch of grid connected hydrogen electrolysis systems operating under dynamic conditions. *Int J Hydrogen Energy* 2020;(xxxx). <https://doi.org/10.1016/j.ijhydene.2020.10.019>.
- [38] Lüke L, Zschocke A. Alkaline water electrolysis: efficient bridge to CO2-emission-free economy. *Chem Ing Tech* 2020;92(1–2):70–3. <https://doi.org/10.1002/cite.201900110>.
- [39] Brauns J, Turek T. Alkaline water electrolysis powered by renewable energy: a review. *Processes* 2020;8(2). <https://doi.org/10.3390/pr8020248>.
- [40] thyssenkrupp. *Hydrogen from large-scale electrolysis*. 2019. p. 8.
- [41] Eichman J, Harrison K, Peters M, Eichman J, Harrison K, Peters M. “Novel electrolyzer applications: providing more than just hydrogen novel electrolyzer Applications: providing more than just hydrogen. 2014. p. 1–24. <https://doi.org/10.2172/1159377>. no. September.
- [42] Bertuccioli L, Chan A, Hart D, Lehner F, Madden B, Standen E. Study on development of water electrolysis in the EU, Fuel cells and hydrogen joint undertaking. *Fuel Cells Hydrog Jt Undert* 2014;1(February):1–160.
- [43] Ulleberg Ø, Nakken T, Eté A. The wind/hydrogen demonstration system at Utsira in Norway: evaluation of system performance using operational data and updated hydrogen energy system modeling tools. *Int J Hydrogen Energy* 2010;35(5):1841–52. <https://doi.org/10.1016/j.ijhydene.2009.10.077>.
- [44] Zondervan E, Grossmann IE, de Haan AB. *Energy optimization in the process industries: unit commitment at systems level*, vol. 28. Elsevier B.V.; 2010. no. C.
- [45] NOW. *Studie IndWEDe*. 2018.
- [46] Gurobi Optimization LLC. *Gurobi optimizer reference manual*. 2020.