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Impact of power supply fluctuation and part load operation on the efficiency of alkaline water electrolysis

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HIGHLIGHTS

• A 6-pulse thyristor model is combined with a dynamic electrolysis model.
• The electrolysis models are suitable for both small-amplitude and large-amplitude ripples.
• Simulations were performed for a lab-scale electrolyser as well as commercial electrolysers.
• At low load ripples can cause up to 10% efficiency loss.
• An optimized L-filter can be used to suppress ripples and efficiency losses.

ABSTRACT

Contrary to traditional electrolysers which operate continuously at their nominal load, future alkaline electrolysers need to be able to operate over a wide load range due to the variability of renewable electricity supply. We have investigated how the residual ripples from thyristor-based power supplies are influenced by the operating load of the system, and how these ripples affect the efficiency of alkaline electrolysers. For this, a simulation tool was developed which combines a six-pulse bridge thyristor rectifier model with closed-loop current control and semi-empirical electrolysis models. The electrolysis models can simulate the potential response to both direct and high amplitude alternating currents for lab-scale and industrial electrolysers. The electrolysis model of the lab-scale electrolyser was validated with experiments with a square wave current input. The models show that without filters the ripples result in a total system efficiency loss of 1.2–2.5% at full load and of 5.6–10.6% at a part load of 20% depending on the type of electrolyser. The implementation of an optimized L-filter suppresses residual ripples and reduces the efficiency losses to 0.5%–0.8% at full load and to 0.8–1.2% at the minimum load.

1. Introduction

The world is striving to transform the energy sector to zero-carbon by 2050 through the mitigation of CO₂ emissions which are intrinsic to the current fossil-based energy sources [1]. Green hydrogen produced by water electrolysis will be a key decarbonisation enabler in a variety of...
seectors including the chemical industry, long distance transport, and steel production [2]. Moreover, green hydrogen is an attractive energy storage medium which can decouple the intermittent renewable electricity supply from demand.

Alkaline water electrolysis is the most cost-effective water electrolysis technology as it combines inexpensive non-noble metal electrodes with long lifespan, and high efficiency [3]. Nonetheless, traditional alkaline electrolyser that have been used on a large scale since the 20th century have certain weaknesses when compared to the other water electrolysis technologies. One limitation is the relatively low operating current density of 0.2–0.4 A cm$^{-2}$ [3], which is attributed to the high ohmic resistance of alkaline electrolyser. This makes that traditional alkaline electrolyser are relatively large, bulky devices. Furthermore, these electrolyser suffer from reverse currents when they are shut down, which can damage electrodes [4]. Another weakness is the restricted minimum partial load of 10–40% [5], which is determined by the hydrogen in oxygen volume fraction [6]. These weaknesses do not provide challenges when coupling these electrolyser with intermittent renewable electricity [3], but these can be overcome through development of advanced electrodes, separators, and optimization of the operating parameters [4]. In recent years more advanced alkaline electrolyser are being developed that are capable of operating at significantly higher current densities and are suitable for operation with intermittent renewable electricity [7].

When considering the water electrolysis process, the power supply to the electrolyser also plays an essential role. Although this part of the electrolyser plant generally receives less attention, the costs of the power supply system are already comparable to the costs of the electrolyser and are expected to be significantly higher in the future as electrolyser costs are expected to fall due to innovations [8]. Therefore, it is of key importance to investigate the most cost-effective power supply option and also to properly understand the interactions between electrolyser and power supply especially for operation at lower loads.

Water electrolysis requires a direct current (DC) supply, while the electricity from the grid and wind farms is alternating current (AC). Therefore, AC-DC rectifiers are utilised to convert the electricity supply to DC [9]. AC-DC rectifiers for electrolyser can be classified according to the type of used semiconductor and controllability [10]. Thyristor-based rectifiers, such as 6-pulse bridge or 12-pulse bridge thyristor rectifiers, are semi-controllable where only turn-on control is possible. In contrast, transistor-based rectifiers such as metal-oxide-semiconductor field-effect transistor (MOSFET), insulated gate bipolar transistor (IGBT), and gate turn-off thyristor (GTO), have full control of the turn-on or off.

Thyristor-based rectifiers are significantly cheaper and have a lower power consumption at nominal load than more advanced power electronics solutions. For this reason, they are still the industrial standard for major industrial electrochemical processes such as chlor-alkali production. However, the costs of green hydrogen are not only driven by the capital costs, but also by the variable costs of the process. In this respect an important question is how the power supply system influences the efficiency of the water electrolysis process. At nominal load all types of rectifiers perform reasonably well resulting in a low ripple factor and a high efficiency, but this changes at partial load, especially for thyristor-based rectifiers. For a 6-pulse bridge thyristor rectifier, the ripple factor was measured to be as high as 71% at a minimum load of 25%, whereas it is only 14% at the nominal load [11]. These ripples can result in a significant decrease in efficiency.

The negative influence of ripples on electrolyser efficiency was shown in several studies [11–16]. In one study the current output of different rectifiers was simulated by a power supply emulator which was connected to a commercial electrolyser. The authors concluded that there is a 10% efficiency increase in alkaline electrolysis when transistor-based rectifiers are used over thyristor-based rectifiers [16]. Another study followed a similar approach and experimentally determined the energy consumption based on a current supply from three different rectifier topologies but with a focus on dynamic operation at different loads [11]. It suggested that using thyristor-based rectifiers with alkaline electrolyser results in up to 13% higher energy consumption when compared to an almost smooth DC output.

In most of these studies the electrolysis process is largely regarded as a “black box”. This makes it difficult to translate the results to larger scale and more advanced types of alkaline electrolyser. Therefore, there is a clear need for an electrolyser model that can be coupled to existing rectifier models.

There are many studies on electrolyser models, but most of them are steady state models that lack the ability to properly describe the dynamic response due to ripples in the supplied current. There are also dynamic models, but they typically assume that the electrolyser behaves as a purely resistive load, not considering any capacitive behaviour [15].

A more advanced dynamic alkaline electrolyser model was built by Urtzia and Sanchis [17], which based their electrolyser model on sixteen empirical coefficients. The model included the thermodynamics, electrodes activation, double layer capacitance, and ohmic resistance contributions and could predict the DC response and the dynamic response due to ripples. The model was further expanded to include a thermal model and a gas cross over model [18]. However, this model does not account for the non-linear behaviour of the polarisation curve, which is relevant for high ripple amplitudes. Also, the model lacks an efficiency analysis of alkaline electrolyser at a variable load operation.

In this study, we will further investigate the interactions of alkaline electrolyser and their power electronics-based power supply. We will investigate the influence of part load operation on both the efficiency of the power supply and the electrolyser. We will do this by modelling both a laboratory scale electrolyser as well as commercial alkaline electrolyser at variable loads and ripple content.

In our electrochemical models we consider both the ohmic and capacitive behaviour. For the laboratory scale electrolyser model, we follow a semi-empirical approach in which electrochemical impedance spectroscopy (EIS) and chronopotentiometry are utilised to characterise the lab-scale alkaline electrolyser. The experimental results are used to construct our model that can predict the effects of both small-signal and large-signal AC ripple amplitudes. This is not straightforward, since EIS is based on small-signal AC perturbations and associated linear responses. This makes large-signal modelling challenging and requires further considerations in the analysis of data, which are further discussed in the Modelling section. For the industrial electrolyser models, models are constructed based on the translation of available performance data into fitted overpotentials and ohmic resistances. The capacitive contributions of the industrial electrolyser were obtained by considering the capacitance of the anode and cathode materials whose values were derived from experiments and the literature.

2. Experimental

2.1. Three-electrode cell

A three-electrode cell with a Luggin capillary was used for EIS measurements with a nickel working electrode, a platinum mesh as the counter electrode, and as a reversible hydrogen reference electrode (Gasketel). The overhead of the three-electrode cell was continuously purged with nitrogen during the measurements. The working electrode was prepared by cutting a 0.3 mm thick perforated nickel sheet (Veco) with a hole diameter of 1 mm, a pitch of 1.5 mm and 99.5% purity into pieces of 2.5 cm × 1 cm (effective geometrical area is 5 cm$^2$, as both sides of the electrode are exposed to the electrolyte). Prior to the measurements the nickel sheets were rinsed with isopropanol and demineralised water. The experiments were conducted using 6 M KOH electrolyte prepared from KOH pellets (VWR Chemicals) and demineralised water (0.067 μS cm$^{-1}$) at room temperature. The electrodes were pre-treated by cyclic voltammetry (CV) scans at 100 mV s$^{-1}$ in the potential range of −0.3 to 1.6 V/RHE for 20 cycles. A potentiostat
(IviumStat.XRe) was used for the EIS experiments and the accompanying software (Iviumsoft) was used for the data acquisition and analysis.

2.2. Flow cell

An in-house 3D printed cell with a zero-gap design (details of the cell are shown in Fig. S2 of the Supplementary Information) was used for EIS and chronopotentiometry experiments. The electrolyte was 6 M KOH prepared from KOH pellets (VWR Chemicals) and demineralised water. The electrodes were 3.5 cm × 2.85 cm of the perforated nickel sheets described in the three-electrode cell section, which were pressed against a ZIRFON PERL UTP 500 (Agfa) diaphragm. The setup has a mixed circuit for the anolyte and catholyte with a single pump circulating the electrolyte at a constant rate of 20 L h⁻¹. The overhead of the anolyte and catholyte gas-liquid separators was continuously purged with nitrogen during the measurements. The electrodes were used for multiple experiments. Prior to their first use they were pre-treated by applying a DC of 0.1 A cm⁻² for 1 h to obtain a stable response. The electrolyser nominal current density was set at 0.2 A cm⁻². The polarisation data for the DC model analysis were obtained by imposing constant currents and measuring the potential response. The currents were applied for 60 s, and the voltage value was taken as the average of the last 15 s. A potentiostat (Ivium Vertex.10A.EIS) was used for the EIS and chronopotentiometry experiments and the accompanying software (Iviumsoft) was used for the data acquisition and analysis.

2.3. Validation experiments

For the validation of the electrochemical model, transient current waveforms and square wave input currents at a frequency of 50 Hz were supplied to the lab-scale electrolyser at 95% and 20% AC amplitude. The experiments were conducted at the nominal load of 0.2 A cm⁻² of the lab-scale electrolyser as well as at partial loads of 50% and 20%. Additionally, sinusoidal current profiles at frequencies of 300 Hz were supplied at AC amplitudes of 95% of the nominal current density of the flow cell.

2.4. Electrochemical impedance spectroscopy

Galvanostatic EIS measurements were conducted at 10% AC perturbation of the DC current value. The measurements were carried out in the frequency range of 1–100,000 Hz at 6 frequencies per decade. The studied current density range was 0.004–0.4 A cm⁻².

2.5. Analysis of EIS data

The data was analysed by fitting the impedance data into an equivalent circuit model. Three-electrode cell data were fitted into a single Randles circuit, which represents a one electrode process. For the flow cell data analysis, two Randles circuits were used to reflect the anodic and cathodic processes with one resistor to model the cell area resistance. An inductive element was added in series to account for the cable inductance. The details of the equivalent circuit fitting and mathematics can be found in Ref. [19]. The Randles equivalent circuit model was used with a constant phase element (CPE) instead of a pure capacitance, since this gave a better fit to the experimental data. Brug’s formula, shown in Eq. (1) [20], was used to extract the double layer capacitance values ($C_{DL, cell}$, $C_{DL, rev}$) (in F cm⁻²) from the CPE values. In this equation, $Q$ is the CPE element (in F cm⁻² s⁻¹), $R_{cell}$ is the ohmic area resistance of the cell obtained via EIS (in Ω cm²), $R_{ct}$ is the charge transfer resistance of the anode or cathode (in Ω cm²), and $N$ is the constant phase exponent (where 0 < N < 1).

$$C_{DL, cell} = Q \left( \frac{1}{R_{ct}} + \frac{1}{R_{cell}} \right)^{\frac{1}{N}}$$

3. Modelling

For our study on the influence of power fluctuation and power quality on the efficiency of alkaline electrolyzers, we utilise the dynamic modelling capabilities of MATLAB-SIMULINK® to combine a power conversion model and an electrochemical model. The model simulates the potential response to a current input which is conditioned from 3-phase AC by an AC/DC rectifier model. The rectifier current output is normalised to current density which has a DC offset $i_{DC}$ in addition to an AC amplitude $i_{AC}$ as shown in Eq. (2). As shown in Fig. 1, the model separates the current input into its AC and DC components by using a running average Eq. (3), where $T$ is the reciprocal of the fundamental frequency (in seconds), and $t$ is the simulation time (in seconds). The constant DC signal is used to calculate the DC potential response while the pure AC ripple signal is used to predict the dynamic potential response.

$$i_{tot} = i_{DC} + i_{AC}$$

$$i_{AC} = \frac{1}{T} \int_{(t-T)}^{t} i_{tot} dt$$

3.1. Electrochemical model

The electrochemical model is based on a DC part that includes the thermodynamic potential, overpotential, and area resistance of the cell as estimated from polarisation curves. Additionally, it contains an AC model which comprises the dynamic response of the electrolyser based on the ohmic resistance, charge transfer resistance, and double layer capacitance values.

This dynamic potential response $E_{cell, DC}$ is added to the DC potential response $E_{cell, AC}$ to obtain the total potential for one cell, which is number up by the number of cells in the electrolyser stack to obtain $E_{cell}$ as shown in Eq. (4), where $N_{cell}$ is the number of cells in a stack.

$$E_{cell} = N_{cell} \left( E_{cell, DC} + E_{cell, AC} \right)$$

The DC potential response $E_{cell, DC}$ is estimated by using a semi-empirical model as shown in Eq. (5.5), which is a simplification of Eq. (5.3). The polarisation data of a lab-scale electrolyser as well as two industrial electrolyzers were fitted to Eq. (5.5) [21], where $E_{cell, DC}$ is the DC potential response (in V), $E_{rev, T, P}$ is the reversible cell potential (in V), $b$ is the combined anodic and cathodic Tafel slopes (in V dec⁻¹), $i_{DC}$ is the DC current density (in A cm⁻²), $i_0$ is a non-linear average of the cathodic and anodic exchange current density (in A cm⁻²), and $R_{ohm}$ is the fitted ohmic area resistance of the cell (in Ω cm²). Prior to data fitting, the $E_{rev, T, P}$ was calculated for the operating temperature and pressure [21]. We would like to remark that no mass transfer related potential contributions are considered in the fitting. Reason is that mass transfer limitations are typically not observed in alkaline electrolyzers, as also evidenced by the absence of any Warburg-type elements in the Nyquist plots.

For the simulation of commercial alkaline electrolyzers, the parameters for the DC model were estimated by fitting available polarisation data of a Lurgi electrolyser [22] and the electrolyser of the BTU Cottbus [23] to Eq. (5.5) (data and analysis shown in Tables S1–S4 in the Supplementary Information).

$$E_{cell, DC} = E_{rev, T, P} + a \ln \left( \frac{i_{DC}}{i_0} \right) + c \ln \left( \frac{i_{DC}}{i_0} \right) + iR_{fit}$$

$$E_{cell, DC} = E_{rev, T, P} + b \ln \left( \frac{i_{DC}}{i_0} \right) + iR_{fit}$$
The AC model was built as an equivalent circuit model and includes two Randles equivalent circuits separated by a resistor $R_{cell}$. Each Randles equivalent circuit contains a charge-transfer area resistance $R_{ct}$ in parallel with a double layer capacitor $C_{dl}$. $R_{ct}$ depends on the heterogeneous kinetic properties of the electrode reaction while $R_{cell}$ describes the cells ohmic area resistance which includes the electrolyte and the separator resistances.

The equivalent circuit elements shown in Fig. 1 require input variables which can be measured via EIS. For the laboratory scale electrolyser, these input variables were determined from equivalent circuit fitting of Nyquist plots at various points in the current density range (see Experimental section). For the industrial electrolysers, the parameters $R_{ct,a}$ and $R_{ct,c}$ were obtained by correlating the charge transfer resistances to the estimated Tafel slopes and the current density as shown in Eqs. (6) and (7) [24]. Since only combined Tafel slopes could be fitted from the polarisation curves, the anodic Tafel slope $a$ was assumed to be 0.04 V based on values reported in the literature [25]. The cathode Tafel slope $c$ was then determined by subtracting the anodic Tafel slope from the fitted combined Tafel slope.

$$g_{ct,a} = \frac{\alpha}{1.0 \ln(10)} \quad (6)$$

$$g_{ct,c} = \frac{c}{1.0 \ln(10)} \quad (7)$$

Several approaches were considered for the implementation of the charge transfer resistances in the model, especially considering that the model should also work for high ripple amplitudes. One approach would be to implement these variables at the direct current density value $i_{DC}$ regardless of the ripple amplitude. This approach only works for small-ripple factors. Averaging was done by numerical integration of the charge transfer current density value, as shown by dashed line (2) in Fig. S5. The averaging procedure applied to the charge transfer resistances in Eq. (8) was not applied for the double layer capacitances (discussed in Fig. 5 in the Results and Discussion section). For the laboratory scale electrolyser, the anodic $C_{dl,a}$ values fitted from the Nyquist plots changed as a function of current density and were therefore implemented as a function of the current density in the model. In contrast, the variation of the cathodic $C_{dl,c}$ with current density was limited and therefore a constant $C_{dl,c}$ value was taken for the whole current density range. For the industrial scale electrolysers, the $C_{dl,a}$ values were assumed to be the same as for the laboratory scale electrolysers, since in both cases nickel electrodes were used. The $C_{dl,c}$ values for the Raney Nickel cathodes were obtained from the literature [26].

$$R_{ct,a}(i_{tot}) = \begin{cases} 
\frac{1}{(i_{DC} - i_{tot})} \int_{i_{tot}}^{i_{DC}} Rct(i_{tot})di_{tot} & i_{tot} < i_{DC} \\
\frac{1}{(i_{tot} - i_{DC})} \int_{i_{DC}}^{i_{tot}} Rct(i_{tot})di_{tot} & i_{tot} > i_{DC} 
\end{cases} \quad (8)$$

The power conversion model simulates a six-pulse bridge thyristor rectifier, and a circuit diagram of the rectifier model is shown in Fig. 1. As can be seen in Fig. 1, the model comprises a thyristor rectifier with a closed-loop proportional-integral (PI) current control by a pulse generator. One power supply was designed for the three electrolysers under study and its specifications are shown in Table 2 (detailed calculations shown in Table S5 in the Supplementary Information). Additionally, a DC inductance smoothing circuit (commonly referred to as an L-filter) is included in the rectifier model to reduce the ripple amplitude. An L-filter is characterised by an inductance value $L_{DC}$ and a resistance value $R_L$. Table 3 summarises different sets of values for the L-filters which were used in the model to study the effect of the ripple amplitude on the
Table 1
Parameters of the simulated electrolyser models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Lurgi Electrolyser [22]</th>
<th>BTU Cottbus Electrolyser [23]</th>
<th>Lab-scale Electrolyser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Current Density</td>
<td>A/cm²</td>
<td>0.165</td>
<td>0.721</td>
<td>0.2</td>
</tr>
<tr>
<td>Electrode Area</td>
<td>cm²</td>
<td>20000</td>
<td>4360</td>
<td>10</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>90</td>
<td>70</td>
<td>25</td>
</tr>
<tr>
<td>Pressure</td>
<td>Bar</td>
<td>30</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Number of cells per stack</td>
<td></td>
<td>–</td>
<td>278¹</td>
<td>290¹</td>
</tr>
<tr>
<td>Anode Material</td>
<td></td>
<td>Perforated Nickel</td>
<td>Perforated Nickel</td>
<td>Perforated Nickel</td>
</tr>
<tr>
<td>Cathode Material</td>
<td></td>
<td>Perforated Nickel</td>
<td>Raney Nickel</td>
<td>Raney Nickel</td>
</tr>
<tr>
<td>Total Tafel Slope (b)</td>
<td>V dec⁻¹</td>
<td>0.04³</td>
<td>0.04⁴</td>
<td>0.04⁴</td>
</tr>
<tr>
<td>Anodic Tafel Slope (a)</td>
<td>V dec⁻¹</td>
<td>0.12⁵</td>
<td>0.07³</td>
<td>0.12⁶</td>
</tr>
<tr>
<td>Cathodic Tafel Slope (c)</td>
<td>V dec⁻¹</td>
<td>0.4⁸</td>
<td>0.4⁸</td>
<td>0.00006⁴</td>
</tr>
<tr>
<td>Double layer capacitance</td>
<td>cm²</td>
<td>0.89</td>
<td>0.41</td>
<td>1.42</td>
</tr>
<tr>
<td>Double layer capacitance</td>
<td>cm²</td>
<td>1.26</td>
<td>1.25</td>
<td>1.23</td>
</tr>
<tr>
<td>Reversible Cell Potential</td>
<td>V</td>
<td>11.9⁸</td>
<td>27⁶</td>
<td>0.082²</td>
</tr>
<tr>
<td>Exchange Current Density</td>
<td>cm²</td>
<td>0.165</td>
<td>0.721</td>
<td>0.2</td>
</tr>
</tbody>
</table>

¹ Number of cells of the Electrolyser of the BTU Cottbus was numbered up to match the production rate of the Lurgi electrolyser in Nm³ hour⁻¹ while the number of cells of the lab-scale electrolyser was numbered up to match the stack voltage range of the other electrolyzers under study.

² Tafel slope and exchange current density values were obtained from fitting the model in Eq. (4) to experimental data.

³ An anodic Tafel slope value of 0.04 V dec⁻¹ was assumed based on values reported in the literature [25]. For the lab-scale electrolyser, a plot of R₆ as a function of i⁻¹ gives a slope of 0.038 V dec⁻¹ (see Fig. S3 in the Supplementary Information).

⁴ The cathodic Tafel slope is calculated by finding the difference between the total Tafel slope b and anodic Tafel slope a.

⁵ The cathodic material is the Raney Nickel whose double layer capacitance value was determined in Ref. [26].

⁶ Experimentally determined via EIS in a lab-scale electrolyser.

⁷ The experimentally determined values are shown in Tables S12-S14.

electrolyser efficiency. It should be noted that the use of the L-filter creates additional power losses in the inductor, which can be calculated via Eq. (9) where ΔP_L is in Watt and t_f is the final simulation time (in seconds). The efficiency loss Δη_L due to the L-filter in Eq. (12) was evaluated by calculating the ratio of the energy loss ΔE_Loss (in Joule) in

Table 2
Specifications of the six-pulse bridge thyristor rectifier designed for the electrolyzers simulations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_L</td>
<td>MW</td>
<td>1.914</td>
</tr>
<tr>
<td>V_DC</td>
<td>V</td>
<td>580</td>
</tr>
<tr>
<td>I_DC</td>
<td>A</td>
<td>3300</td>
</tr>
<tr>
<td>i_appDC</td>
<td>Hz</td>
<td>50</td>
</tr>
<tr>
<td>i_thermDC</td>
<td>Hz</td>
<td>300</td>
</tr>
<tr>
<td>E_L</td>
<td>V</td>
<td>430</td>
</tr>
<tr>
<td>V_AC,max</td>
<td>V</td>
<td>650</td>
</tr>
<tr>
<td>L_AC × 10⁸</td>
<td>H</td>
<td>4.6</td>
</tr>
<tr>
<td>R_AC × 10⁴</td>
<td>Ω</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Table 3
Specifications of the L-filters used in the simulation.

<table>
<thead>
<tr>
<th>Number</th>
<th>L_DC (H) × 10⁸</th>
<th>R_L (Ω) × 10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.3</td>
<td>28.8</td>
</tr>
<tr>
<td>2</td>
<td>9.77</td>
<td>18.4</td>
</tr>
<tr>
<td>3</td>
<td>6.25</td>
<td>11.8</td>
</tr>
<tr>
<td>4</td>
<td>4.04</td>
<td>7.54</td>
</tr>
<tr>
<td>5</td>
<td>2.05</td>
<td>3.86</td>
</tr>
<tr>
<td>6</td>
<td>1.31</td>
<td>2.47</td>
</tr>
<tr>
<td>7</td>
<td>1.05</td>
<td>1.98</td>
</tr>
<tr>
<td>8</td>
<td>0.839</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Eq. (10) to the total energy \( E_{\text{stack}} \) (in Joule) as shown in Eq. (11).

\[
\Delta P_L = I_L^2 \cdot R_L
\]  

(9)

\[
\Delta E_{\text{Loss}} = \int_0^{t_f} \Delta P_L \, dt
\]  

(10)

\[
E_{\text{stack}} = \int_0^{t_f} E_{\text{app}} \cdot I_{\text{DC}} \, dt
\]  

(11)

\[
\Delta \eta_L = \frac{\Delta E_{\text{Loss}}}{E_{\text{stack}}}
\]  

(12)

The ripple amplitude is characterised by the ripple factor (RF), which is the ratio of the root mean square of the AC signal \( i_{\text{AC,RMS}} \) to the DC signal \( i_{\text{DC}} \) as shown in Eqs. (13) and (14).

\[
i_{\text{AC,RMS}} = \sqrt{\frac{1}{T} \int_{-T}^{T} i_{\text{AC}}^2(t) \, dt}
\]  

(13)

\[
RF = \frac{i_{\text{AC,RMS}}}{i_{\text{DC}}} \times 100\%
\]  

(14)

3.3. Efficiency calculation

The efficiency of water electrolysis is the ratio of the amount of energy required to split a water molecule into oxygen and hydrogen to the actual energy used. The thermal energy efficiency \( \eta_{\text{therm,DC}} \) for a DC current without ripples can be calculated via Eq. (15), where \( E_{\text{th}} \) is the thermoneutral potential (in V). When the input current contains residual ripples, the total cell potential response \( E_{\text{tot}} \) varies with time. The average stack efficiency \( \eta_{\text{sect,DC}} \) can then be estimated by evaluating the ratio of the required power to the actual power consumption over time. This is shown in Eq. (16) where the time varying components \( E_{\text{app}}(t) \) and \( E_{\text{tot}}(t) \) are integrated over time up to the final simulation time \( t_f \).

\[
\eta_{\text{sect,DC}} = \frac{E_{\text{app}}}{E_{\text{DC}}}
\]  

(15)
The rectifier losses were calculated analytically in accordance with the IEEE Standard 1158–1991 [27] (calculations shown in Eqs. (S1) and (S2) in the Supplementary Information). These losses are mainly conduction losses from the thyristor semiconductors and a constant efficiency of 99.7% was found for the rectifier. This efficiency value was used in the calculation of the total system efficiency shown in Eq. (17). In practice, higher efficiency losses of 2–3% are expected from the voltage step down in the transformer (from 10 kV to 650 V), but these are not considered in this study. The total system efficiency is subtracted from the efficiency at DC potential calculated in Eq. (15) to give the efficiency loss shown in Eq. (18).

\[
\eta_{\text{rectifier}} \times (1 - \Delta \eta) \times \eta_{\text{system}}
\]

(17)

\[
\eta_{\text{total}} = \eta_{\text{stack}} - \eta_{\text{system}}
\]

(18)

### 4. Results and discussion

#### 4.1. Determination of model variables

Fig. 2 shows the polarisation data for the lab-scale flow cell, the Lurgi electrolyser, and the BTU Cottbus electrolyser. The DC model in Eq. (3) was fitted to this data to extract the DC model variables, which were for the lab-scale electrolyser a Tafel slope \( b = 0.16 \text{ V dec}^{-1} \), exchange current density \( i_0 = 8.1 \times 10^{-7} \text{ A cm}^{-2} \), and a fitted area cell resistance \( R_{\text{cl}} \) of 1.42 \( \Omega \text{ cm}^2 \) (fitting results for the industrial electrolyzers are shown in Tables S3 and S4). These fitted variables are in line with values reported in the literature with combined Tafel slope \( b \) ranging between 0.146 and 0.176 \text{ V dec}^{-1}, and average exchange current density \( i_0 \) ranging between 0.41 \( \times 10^{-7} \) and 164 \( \times 10^{-7} \text{ A cm}^{-2} \) [25, 28–36].

The AC model variables were determined via EIS experiments in the zero-gap flow cell. Fig. 3 shows complex plane plots at different current densities including the nominal current density and the maximum and minimum current density at 95% AC amplitude. Plots at more current densities including the nominal current density and the maximum and minimum current density at 95% AC amplitude. Plots at more current densities are shown in Fig. S4 of the Supplementary Information. Two semicircles can be identified since the time constants \( R_{\text{ct}}C_\text{dl} \) of the anode and cathode differ sufficiently. The value of \( R_{\text{ct}}C_\text{dl} \) can be obtained from the frequency at the peak of the semicircles \( (R_{\text{ct}}C_\text{dl} = 1/2\pi f_0) \). By assigning the first semicircle to HER and the second semicircle to OER, the equivalent circuit parameters can be found. This allocation is justified by considering that the double layer capacitance during the HER is smaller than that during the OER (see following discussion on three-electrode cell experiments). This difference is more pronounced at low current densities where the difference in double layer capacitance values is larger.

Fig. 4 compares the behaviour of the cell area resistance \( R_{\text{ct}} \) and the anodic \( R_{\text{ct,a}} \) and cathodic \( R_{\text{ct,c}} \) area charge transfer resistances that were derived from the EIS data. The cell area resistance was found to be largely independent of the current density value and hence one average value of 0.96 \( \Omega \text{ cm}^2 \) was used in the lab-scale model. In contrast, the charge transfer resistances are inversely proportional to the current density value and this dependence was implemented in the AC model via Simulink lookup tables. The Simulink tables contained \( R_{\text{ct,avg}} \) variables obtained from EIS measurements for the lab-scale model, while modelled data were used for the industrial electrolyzers as calculated from Eqs. (6) and (7).

Three electrode cell experiments allow the individual investigation of anode and cathode. Fig. 5 compares the double layer capacitance values obtained in a flow cell and a three-electrode cell (EIS equivalent circuit fits from the three-electrode setup are shown in Tables S10 and S11 in the Supplementary Information). It shows that the double layer capacitance is much higher for the oxygen evolution reaction (OER) than for the hydrogen evolution reaction (HER). Moreover, the double layer capacitance in the HER region \( (C_{\text{dl,a}}) \) is seemingly independent of the current density, contrary to the OER double layer capacitance \( (C_{\text{dl,c}}) \), which shows a significant dependence on current density. The dependence on current density has been attributed to a pseudocapacitance caused by the thickness of the oxide layer formed on the metallic surface prior to the OER, which is removed during the oxygen evolution at higher current densities [37, 38]. The obtained values of the double layer capacitance in the OER region from three-electrode cell measurements are in line with values reported by Lyons and Brandon [25], who used the elaborate Armstrong-Henderson equivalent circuit model to distinguish between the metallic capacitance and the pseudocapacitance of nickel in NaOH at the OER region.

Previous studies in the literature suggest values of 40–48 \( \mu \text{F cm}^{-2} \) [39, 40] for nickel in the HER region, which agree with our HER region’s three-electrode measurements averaged at 44 \( \mu \text{F cm}^{-2} \) (values shown in Table S11 in the Supplementary Information). As can be seen in Fig. 5, the double layer capacitance values from flow cell measurements are higher than what is obtained using three-electrode cell measurements for the same electrodes type. This difference is more pronounced in the OER region, which could be caused by the aging of the electrodes in the flow cell, whereas new electrodes were used in the three-electrode setup. The effect of nickel electrodes aging in KOH on the oxide layer structure has been studied previously [41]. In general we would like to emphasize the complex nature of nickel surfaces, which are prone to processes such as the formation of hydrides, different types of hydroxides and oxides and the incorporation of electrolyte impurities. These can significantly influence the double layer capacitance and therefore it is not surprising that we see a significant variation in double layer capacitance values especially for the anode.

In our model, an average value of 64 \( \mu \text{F cm}^{-2} \) was used for the cathodic double layer capacitance \( (C_{\text{dl,c}}) \) while the anodic double layer capacitance \( (C_{\text{dl,a}}) \) was implemented as a function of current density via the use of Simulink lookup tables. Tables S12–S14 in the Supplementary Information summarise the input variables of the lab-scale electrolyser model as a function of current density for the three different loads (20%, 50%, 100%).
4.2. Electrochemical model validation

In this section we validate our electrochemical model by supplying a transient input current to the lab scale electrolyser and comparing the results to our electrochemical model. Fig. 6 compares the square wave potential responses of the lab scale electrolyser and the electrochemical model at the nominal current density and 95% ripple factor (validation results at different conditions are shown in Figs. S6–S9 in the Supplementary Information). The validation results show that the model can accurately predict the potential responses at different load conditions, ripple factors, and frequencies. Therefore, these validation experiments give confidence in the results of the combined rectifier-electrochemical model shown in the simulation results.

4.3. Lab-scale electrolyser simulations

Fig. 7 compares the total system efficiency loss relative to the pure DC efficiency of the lab-scale electrolyser as a function of ripple factor accurately predict the potential responses at different load conditions, ripple factors, and frequencies. Therefore, these validation experiments give confidence in the results of the combined rectifier-electrochemical model shown in the simulation results.
for operation at 20%, 50% and 100% load. Detailed efficiency simulation results are shown in Tables S15–S17 in the Supplementary Information. The results are based on the double layer capacitances as measured with the flow cell. Since especially for the anode there was a large discrepancy of the double layer capacitance between the flow cell and the three-electrode cell, we also made some simulations with the double layer capacitance values as measured with the three-electrode cell (see Fig. S10), yet the differences were limited.

It can be seen that the efficiency losses without an L-filter are significant, especially for operation at 20% load. This incentivises the inclusion of L-filters although they weigh heavily on the cost of the rectifier. As shown in Fig. 7, the properties of the L-filter determine to what extent the residual ripples are suppressed.

When considering the total system of power supply and electrolyser, the highest performing L-filters do not achieve the lowest efficiency loss although they reduce the ripple factor to a minimum. The reason for this is that the efficiency loss from the higher performing filters exceeds the electrolyser’s ripple caused efficiency losses. The optimum where the total efficiency loss is at a minimum differs between operating loads. The optimum for the lab-scale electrolyser at full load would be L-filter 5 while the minimums at 50% and 20% loads are at L-filters 4 and 2, respectively. This difference in minimums is attributable to higher electrolyser efficiency losses at partial loads caused by an increase in the ripple factor relative to a full load operation. Conversely, the L-filters cause a lower efficiency loss at lower loads as expected from Eq. (6).

To select the optimum L-filter, a trade-off should be made considering full load operations as well as partial load operations. In practice this will depend on the expected operating profile of the electrolyser. In general L-filter 4 seems to be a good choice, performing reasonably well at both high and low loads.

4.4. Commercial electrolyser simulations

Fig. 8 compares the total efficiency losses of the lab-scale electrolyser to the industrial-scale electrolysers at 50% load operation (the 100% and 20% load scenarios are shown in Figs. S11 and S12 in the Supplementary Information). The three systems show small differences in ripple factors indicating that the ripple factor is only slightly influenced by the differences between these electrolysers. Yet, the BTU Cottbus electrolyser shows higher efficiency losses than the other systems, which suggests that the electrolysers specifications affect the sensitivity to the ripple factor. Compared to the other electrolysers the BTU Cottbus electrolyser has a lower Tafel slope and cell area ohmic resistance, which enables higher current density operation. It might seem counterintuitive that the highest performing electrolyser suffers more efficiency losses than lower performing ones at the same ripple factor. Yet, it can be explained in terms of the relative contribution of the ohmic overpotential to the total cell potential, which is higher for the BTU Cottbus electrolyser (see Figs. S17 and S18 in the Supplementary Information). For the ohmic overpotential all ripples directly lead to efficiency losses. In contrast, the kinetic charge transfer resistances $R_{ct}$ occur in parallel to the double layer capacitance of the electrodes which means that especially at high frequencies the double layer capacitances can “absorb” part of the ripples resulting in a lower efficiency loss.

5. Conclusion

In this study we have investigated the influence of residual ripples from a thyristor-based power supply on the efficiency of alkaline electrolysers at variable load operations. We developed and validated a
simulation tool that couples the power conversion and the electrochemical domains of an electrolysis plant, making the analysis of the interactions between these domains possible. Our simulations showed that low operating loads bring challenges to the use of thyristor-based power supplies which necessitates the use of harmonic filters. However, the selection of these L-filters is not straightforward, and trade-offs need to be made to achieve an optimum system design that considers efficiency losses at different loads. With an optimized filter the efficiency loss at a minimum operating load of 20% can be kept between 0.8% and 1.2% for the different investigated electrolyser types. Yet, these filters come at a cost, and inflict relatively high efficiency losses due to the filter itself when the electrolyser are operated at full load.

We realise that our results are not directly representative for large-scale industrial electrolyser systems since these typically operate with 12-pulse or 24-pulse thyristor rectifiers. The higher number of pulses will result in a lower ripple factor and hence lower efficiency losses. Nevertheless, the same principles do apply and especially at low loads efficiency losses will be significant if no filtering is applied. Although our work has only focused on alkaline electrolysis, the main conclusions will also apply to other types of electrolysis, such as PEM water electrolysis. For PEM a similar electrolyser description with two Randles circuits and a resistor as shown in Fig. 1 can be made. This means that also PEM will suffer significant efficiency losses at low loads if thyristor-based rectifiers are used. This is especially relevant since PEM electrolysis is often portrayed as the most suitable electrolysis technology for flexible operation.

Our work raises the question whether thyristor-based power supplies will be the run on variable renewable electricity, even though they are the cheapest. Advanced transistor-based power supply solutions significantly reduce the ripple factor without the need for a harmonic filter on the DC side. They also do not suffer from significant efficiency losses at low loads. These advantages could offset their higher price. Therefore, the switch from “baseload” electrolyser to variable load electrolyser could be an incentive for replacement of thyristor-based rectifiers with transistor-based rectifiers.

CRediT authorship contribution statement

Senan F. Amireh: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. Niels N. Heineman: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation. Paul Vermeulen: Conceptualization, Resources, Writing – review & editing, Supervision. Rodrigo Lira Garcia Barros: Conceptualization, Methodology, Investigation, Resources, Data curation, Writing – review & editing, Supervision. Dongsheng Yang: Conceptualization, Methodology, Software, Validation, Resources, Writing – review & editing, Supervision. John van der Schaaf: Conceptualization, Supervision, Project administration. Mathes H. T. de Groot: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Supervision, Project administration.

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.

Data availability

The data is available on Mendeley data repository. The DOI is https://data.mendeley.com/datasets/5ynf9xbbs9/1.


