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Development of a mathematical model to calculate the energy savings and the system running costs through hydrogen recovery in wastewater electrolysis cells

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ABSTRACT

Electrooxidation of wastewater using a wastewater electrolysis cell is known to effectively oxidize persistent organics. However, like other chemical physical treatment methods, the treatment costs are high. The separation of the evolving hydrogen using a diaphragm and the subsequent use of it can help to lower the operational costs of such systems. This paper provides a theoretical basis of the benefits of hydrogen recovery in wastewater electrolysis cells using a diaphragm. The paper discusses all main parameter contributing to the energy demand of the cell as well as to the energy saving potential through hydrogen recovery. The paper lays the theoretical foundation for qualified experiments and is meant to stimulate researchers to proof the proposed concept. The calculations show a maximum theoretical energy saving potential of 45% through the recovery of hydrogen at a minimum cell potential of 2.8 V. The calculations also highlight, that the theoretical energy recovery proportion decreases with rising cell potential as the energy demand of the cell depends on the cell voltage, the hydrogen production rate however does not. In summary, it can be concluded that hydrogen recovery in wastewater electrolysis cells is an effective way of reducing the operational costs and increasing the economic feasibility of electrooxidation systems. Finally, the running costs of the system are compared to wastewater disposal costs.

Keywords: Hydrogen; Wastewater electrolysis cell; Diaphragm; Boron-doped diamond electrodes; Oxidation of organics

1. Introduction

Electrochemical wastewater oxidation can be an economically feasible alternative for the treatment of industrial wastewater streams in comparison to conventional disposal pathways. The treatment costs however depend on multiple system parameters like the current density, the cell voltage, and the hydrogen reaction efficiency. Various studies focus on the optimization of the current efficiency in regards to the anodic oxidation efficiency, an economic assessment of the technology however is not yet done [1,2]. Only a few publications consider the recovery of the evolving hydrogen as a potential source to minimize the operation costs by providing hydrogen as a fuel for various applications [3–5]. Possible applications for the recovered hydrogen depend primarily on the generated volume and the hydrogen purity.

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In the absence of cathodic scavenger components, the chemical oxygen demand (COD) load of the wastewater is directly proportional to the produced hydrogen volume. In a typical undivided wastewater electrolysis cell (WEC) the electrode distance is in the range of a few millimeters in order to keep the ohmic losses caused by the wastewater as low as possible. Mixing of the evolving gases can only be prevented by the implementation of a separator between the electrodes. The purity of the hydrogen depends on the type and effectiveness of the used separator. In alkaline water electrolysis, porous separators, so called diaphragms are used to divide electrochemical cells into a catholyte and anolyte space to prevent the mixing of gases. In electrochemical wastewater oxidation systems, separators are rarely used until today, as there is little knowledge about the effects. This article aims to provide a mathematical foundation to calculate the energy-saving potential through hydrogen recovery by means of the implementation of a diaphragm. The article also offers simulation results based on the proposed mathematical equations in order to give hints on the effects of various system parameters on the energy demand of the cell and the resulting running costs of the system.

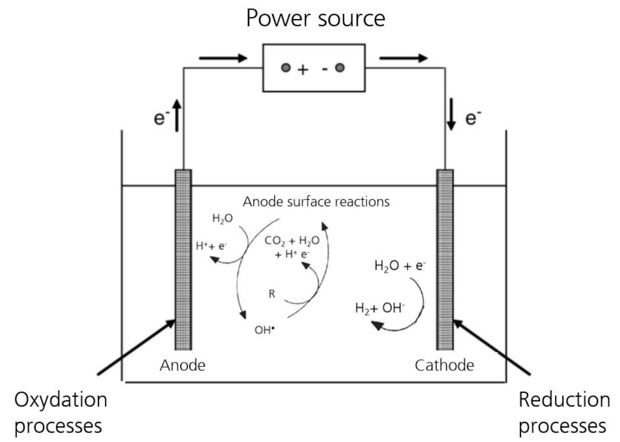

Fig. 1. Schematic illustration of the working principle of a wastewater electrolysis cell.

2. Materials and methods

2.1. Theoretical assumptions and simulation methods

The simulations done in this paper are based on a typical wastewater electrolysis cell as it can be commercially purchased, for example, from DiaCCOn GmbH, Germany. The cell consists of at least two electrodes placed opposite to each other. Typical electrode spaces are 2 mm; separators are usually not placed between the electrodes. When an external power source is applied, water will be reduced at the cathode forming hydrogen gas and hydroxyl ions. Unlike in a conventional electrolysis cell, water will be oxidized forming hydroxyl radicals and not oxygen at the anode. For this, special electrodes with a high overpotential for oxygen are used. The generated hydroxyl radicals finally oxidize the organics in the wastewater via radical reaction mechanisms [1]. The working principle of such a cell is illustrated in Fig. 1. As a basis of the here proposed mathematical model serves the kinetic model of the electrochemical mineralization of organics described by Kapałka et al. [6]. In this widely accepted model, the rate of the mineralization reaction does not depend on the chemical nature of the organic compound present in the wastewater and is mediated through the formation of hydroxyl radicals at the anode according to the reactions given in Fig. 1 [6]. The anodic current efficiency according to this model is only a function of the applied current and the concentration of the organic compounds in the wastewater. The proposed kinetic model differentiates two different operations regimes, namely the current limited control regime and the mass transport control regime. In the current limited control regime, organic compounds are at all times at the vicinity of the anode surface ready to be oxidized and the applied current is the limiting factor. Side reactions do not occur and the current efficiency in regards to the anodic oxidation is 100%. With proceeding electrochemical mineralization of the organic compounds in the wastewater at a constant applied current, the concentration of the organics will decrease to a level, where mass transport effects of the organic compounds to the anode will eventually govern the mineralization velocity of the same. A part of the applied current will in this case not lead to the oxidation of organics, but induce side reactions resulting in the formation of oxygen and thus diminish the anodic current efficiency in regards to the organic mineralization. In case of complete depletion of the organics in the wastewater, only oxygen will be produced at the anode and the current efficiency in regards to the organic mineralization will be zero. Usually, in water science, the chemical oxygen demand instead of the concentration of the individual organic compounds is used to evaluate the overall amount of organics in wastewater. This way, even wastewater consisting of various organic compounds in different concentrations can be characterized and compared easily. A mathematical relation between the concentration of the organic compounds in the wastewater and the COD value of the wastewater is given in [7]. One might suppose that there is an influence of the nature of organic pollutants on the mineralization efficiencies. However, this assumption can be rebutted through various experiments [6]. The current efficiency is therefore independent of the chemical composition of the organic compound and only depends on the applied current and the COD concentration. The composition of wastewater could, however, affect the overall wastewater electrolysis cell efficiency due to precipitation of intermediates or the presence of settable compounds leading to a reduced active electrode surface or the clogging of the cell. Due to this, the provided results in this article refer only to wastewater without settable compounds. Neither are precipitation effects on electrodes taken into account.

The electrolyte conductivity is crucial for the achievable cell voltage and therefore for the energy demand of the system. Where, in classical water electrolysis, the conductivity of the electrolyte has to be increased to run the electrolysis economically efficient, the conductivity of industrial wastewaters is often already in the range of 10–100 mS cm^{-1} as can be seen in Fig. 2 and is therefore already sufficient to achieve low cell voltages. The simulations are carried out for 10 and 50 mS cm^{-1}, respectively, for each parameter considered in

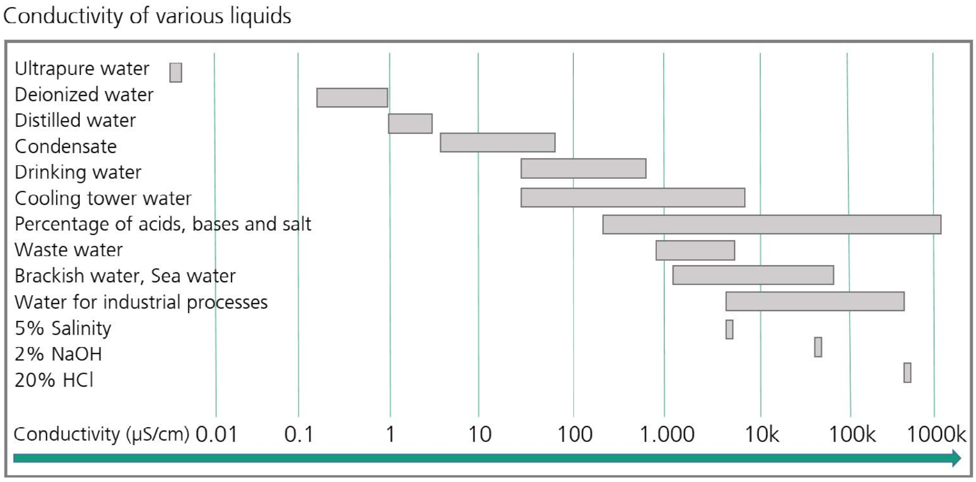

Fig. 2. Comparison of electrical conductivities of various liquids.

this manuscript, representing typical wastewater conductivities suitable for this technology.

A high conductivity and maximum anodic oxidation efficiency are the base to run a wastewater electrolysis cell efficiently. However, the recovery of hydrogen offers the chance to cut back the running costs significantly. Precondition for a maximum hydrogen recovery is a high hydrogen evolution at the cathode. In a conventional water electrolysis cell with no reactive species in the electrolyte only oxonium ions or water molecules will be reduced to form hydrogen. Competitive reactions will not take place. Electrode materials are chosen to yield the highest hydrogen evolution reaction efficiency based on Sabatier's principle [8]. However, in a wastewater electrolysis cell, the hydrogen evolution reaction efficiency η_{HER} depends next to the used electrode material strongly on the wastewater matrix. Furthermore, the electrode must be stable in harsh environments and wide pH-ranges and also should be cheap. Therefore, Ni-doped stainless steel electrodes are commonly used in WEC as these combine those qualities [3]. In pure water without reactive species stainless steel electrodes can achieve η_{HER} up to 80%. However, organic compounds can lead to either a diminishing or an improvement of the hydrogen evolution through either electron scavenging or donation. Whether a certain compound tends to promote or diminish hydrogen evolution, depends on the chemical composition and the formed intermediates during the electrochemical oxidation. To improve the overall cell efficiency, conductive salts like sodium chloride, sodium sulfate, sodium bicarbonate, and sodium nitrate are often added as they increase the electrical conductivity of the wastewater [9]. However, some of the salts form active species, which diminish hydrogen evolution through electron shuttling between the anode and the cathode. A certain fraction of electrons flowing from the anode to the cathode is consumed this way and not available for the reduction of protons or water molecules to form hydrogen [10]. On the other hand, in case of the presence of both, active species, for example, active chlorine and organic compounds in the wastewater no hydrogen evolution reduction will be observed, as the organic compounds act as scavengers for those active species [3]. Taking this into account, it is obvious that the hydrogen evolution reaction efficiency will be unique for each wastewater and could even vary for the same wastewater during the treatment due to the occurrence of active species or intermediates. Efficiency values given in literature vary between 40% and 80% for the regarded wastewater [10–12]. The simulations done in this paper take hydrogen evolution reaction efficiencies between 50% and 100% into account, covering the given values for the most part.

It should be stated here again, that the simulations and calculations carried out in this paper are based on a WEC as described above. The gained results may not apply to different cell designs or wastewaters outside the here defined ones.

The open source cross-platform Spyder, an integrated development environment (IDE) for scientific programming in the Python language, is used for the simulations carried out within this article (Spyder version 3.3.1, Python version 3.7.0). The simulations were conducted based on the mathematical description shown in the subsequent chapter.

2.2. Theory/calculation

The here presented treatment costs do only account for the direct running costs of a wastewater electrolysis cell. Investment costs for the system as well as any further costs are not considered.

2.2.1. Specific electrochemical wastewater treatment costs without hydrogen recovery

The specific wastewater treatment costs depend on various system parameters. Kraft et al. [13] present a mathematical model to calculate the specific electricity running costs ($C_{E(\mathrm{COD})}$) in € kg $_{\mathrm{COD}}{}^{-1}$ of wastewater electrolysis cells in regards to the COD reduction:

$$C_{E(\mathrm{COD})} = \frac{P_{\mathrm{COD}} \times \left(U_{\mathrm{EC}} + \frac{\left(jxd\right)}{\Lambda} \right)}{0.2985 \frac{\mathrm{gO_2}}{\mathrm{Ah}} \times \eta_{\mathrm{OX}} \times 10^3} \times \mathrm{EC}\left(\text{€}\,\mathrm{kg}_{\mathrm{COD}}{}^{-1} \right) \tag{1}$$

where P_{COD} is the eliminated COD (g O_2), U_{EC} is the voltage necessary to produce hydroxyl radicals (V), j is the current density (mA $(cm^2)^{-1}$), d is electrode distance (cm), Λ is conductivity (mS cm^{-1}), η_{OX} is the current efficiency for COD removal, and EC is the electricity cost (€ kWh^{-1}).

Replacing the P_{COD} with the COD concentration of the wastewater c_{COD} (kg O_2 $(m^3)^{-1}$) in Eq. (1), the specific running costs in regards to the COD concentration of the wastewater $C_{E(m^3)}$ can be calculated:

$$C_{E\left(m^3\right)} = \frac{c_{COD} \times (U_{EC} + \frac{\left(j \times d\right)}{\Lambda}}{0.2985 \frac{gO_2}{Ah} \times \eta_{OX}} \times EC\ (€\ (m^3)^{-1}) \quad (2)$$

2.2.2. Specific electrochemical wastewater treatment costs with hydrogen recovery

Hydrogen evolution according to Faraday's law is ideally proportional to the electrical charge $Q_{(COD)}$ needed for COD removal:

$$Q_{(COD)} = \frac{c_{COD} \times 10^3}{0.2985 \frac{gO_2}{Ah} \times \eta_{OX}} \left(Ah\left(m^3_{wastewater}\right)^{-1}\right) \quad (3)$$

The specific volumetric hydrogen production can be calculated by means of the Faraday equivalent $\ddot{A}_{eH_2}$ (g_{H_2} Ah^{-1}) for hydrogen, the hydrogen density ρ (g L^{-1}) and the hydrogen evolution reaction efficiency η_{HER} (%):

$$V_{H_2} = \frac{Q_{COD} \times \frac{\ddot{A}e_{H_2}}{\rho_{H_2}}}{10^3} \times \eta_{HER} \left(m^3H_2\left(m^3_{wastewater}\right)^{-1}\right) \quad (4)$$

The specific energy recovery E_{H_2} (kWh) is given by the multiplication of the volumetric hydrogen production V_{H_2} ($m^3_{H_2}$) and the higher heating value for hydrogen HHV_{H_2} (kWh $(m^3_{H_2})^{-1}$).

$$E_{(H_2)} = V_{H_2} \times HHV_{H_2}\left(kWh\right) \quad (5)$$

Combining Eqs. (2), (3), and (5), the specific wastewater treatment costs with hydrogen recovery as a function of the oxidation and hydrogen evolution reaction efficiencies can be written as follows:

$$C_{E,H_2\left(m^3\right)} = \frac{Q_{COD} \times \left(\left(U_{EC} + \frac{\left(j \times d\right)}{\Lambda}\right) - \frac{\ddot{A}e_{H_2}}{\rho_{H_2}} \times \eta_{HER} \times HHV_{H_2}\right)}{10^3} \times EC((€\ m^3)^{-1}) \quad (6)$$

2.2.3. Theoretical energy-saving potential through hydrogen recovery

By means of Eq. (5) and the cell voltage U (V), the degree of energy-saving through hydrogen recovery $E_{WEC\text{-}H_{2,theoretical}}$ (%) is given by:

$$E_{WEC\text{-}H_{2,theoretical}} = \frac{E_{(H_2)}}{U} \times 100\left(\%\right) \quad (7)$$

with

$$U = \left(U_{EC} + \frac{\left(j \times d\right)}{\Lambda}\right)\left(V\right) \quad (8)$$

2.2.4. Effects of separator on the theoretical energy savings through hydrogen recovery

The implementation of a porous separator introduces an additional electrical resistance R_{Sep} (Ω cm^2), which will decrease the theoretical energy recovery rate depending on the geometrical and electrical properties of the separator. The electrical resistance of the separator can be written as additional voltage U_{Sep} (V), depending on the current density applied to the system, the separator thickness d_{Sep} (mm), and the conductivity of the electrolyte:

$$U_{Sep} = \frac{R_{Sep} \times j}{10^3} + \frac{\left(j \times d_{Sep}\right)}{\Lambda}\left(V\right) \quad (9)$$

The energy savings through hydrogen recovery with consideration of the electrical resistance of the separator $E_{WEC\text{-}H_{2,real}}$ (%) can be written as:

$$E_{WEC\text{-}H_{2,real}} = \frac{E_{(H_2)}}{U + U_{Sep}} \times 100\left(\%\right) \quad (10)$$

3. Results

The results are illustrated using contour plots. By means of that type of graph, it is possible to show the influence of two variables on the results at the same time instead of only one variable. The variables are plotted on the x- and y-axis, respectively. The result is represented in form of a colored contour within the diagram; the associated legend is placed on the right side of the plot.

3.1. Specific electrochemical wastewater treatment costs without hydrogen recovery

Figs. 3 and 4 show the specific running costs for the electrooxidation (EO) of organics in a wastewater electrolysis cell based on Eq. (2) for varying COD current efficiencies and electrolyte conductivities of 10 and 50 mS cm^{-1}, respectively.

The running costs for such a cell with oxidation efficiencies of a 100% (as it can be reached in the current controlled mineralization regime) and a cell voltage of 5 V vary from 0 to about 250 € m^{-3} wastewater with COD levels from 0 to 100 kg $(m^3)^{-1}$. If an electrolyte with higher conductivity is used the decreased cell voltage will lead to running costs from 0 € to about 180 € per cubic meter for the same COD concentrations. Furthermore, it can be seen, that the lower the oxidation efficiency, the higher the treatment costs.

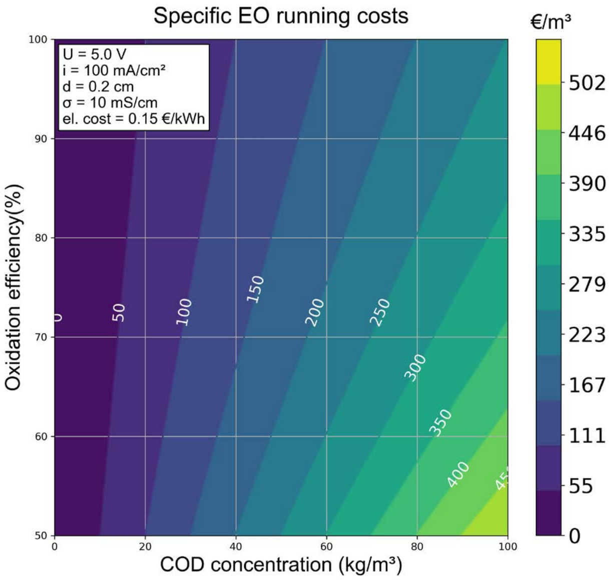

Fig. 3. Specific running costs. Conductivity 10 mS cm^{-1}.

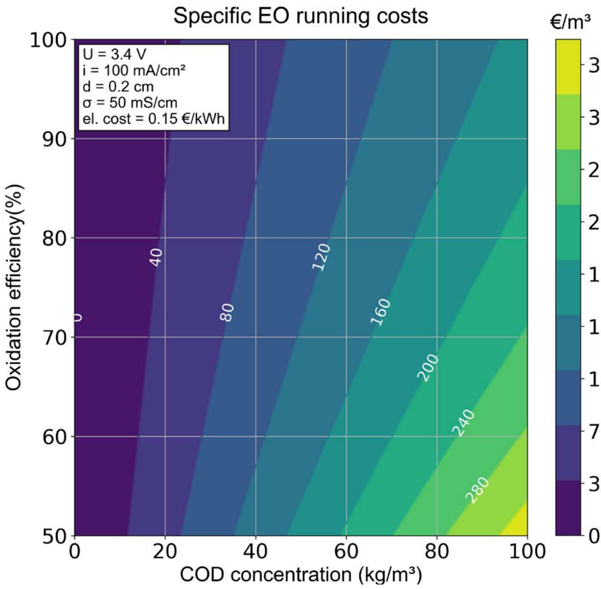

Fig. 4. Specific running costs. Conductivity 50 mS cm^{-1}.

3.2. Theoretical energy saving potential through hydrogen recovery

Hydrogen evolving at the cathode during wastewater treatment can be theoretically recovered to gain back a portion of the required energy.

Fig. 5 illustrates the theoretical energy recovery rates as a function of the wastewater electrochemical cell voltage. The Fig. 5 illustrates, that the higher the required cell voltage necessary for the wastewater treatment, the lower the fraction of energy which can be regained through hydrogen recovery. In addition to that, the lower the hydrogen evolution efficiency is, the lower is the possible energy recovery. Maximum energy recovery of about 45% can be reached at a minimum cell voltage of about 2.8 V and a 100% hydrogen evolution efficiency.

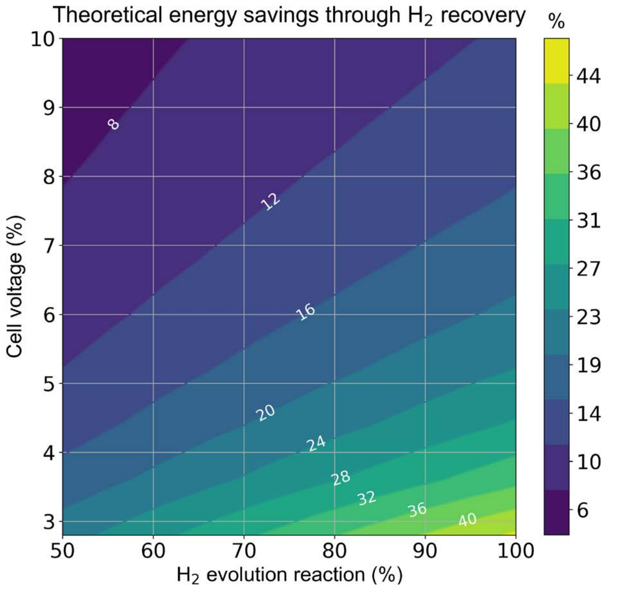

Fig. 5. Theoretical energy-saving potential through hydrogen recovery.

3.3. Effects of a diaphragm on the theoretical energy savings through hydrogen recovery

Efficient hydrogen recovery in a wastewater electrolysis cell requires the implementation of a diaphragm between the electrodes to prevent the mixing of the evolving gases. The implementation of such a diaphragm will inevitably lead to an increase of the electrode distance, thus contributing to a higher electrolyte resistance. The influence depends mainly on the electrode distance, the current density, and the electrolyte conductivity. With increasing electrode distance, the voltage drop caused by the ohmic resistance of the electrolyte increases linearly reaching almost 10 V for an electrolyte conductivity of 10 mS cm^{-1} and almost 2 V at an electrolyte conductivity of 50 mS cm^{-1}. The electrical properties of the used diaphragm material will also cause an additional electrical resistance. The drop in voltage is, in this case, caused by the specific electrical resistance of the used diaphragm and depends on the applied current density. The voltage drop is linear to the specific resistance of the diaphragm, causing voltage drops between 10–50 mV for specific resistances of 100–500 mΩ cm² at a current density of 100 mA (cm²)$^{-1}$.

The implementation of the diaphragm will lead to an additional voltage depending on the electrolyte conductivity witch adds up to the cell potential for the undivided WEC. In analogy to the theoretical recovery potential, the higher the required cell voltage necessary for the wastewater treatment, the lower the fraction of energy which can be regained through hydrogen recovery. In addition to that, the lower the hydrogen evolution efficiency, the lower the possible energy recovery will be. Maximum energy recovery rates of about 36% and 40% can be reached for a minimum cell voltage of about 2.8 V and a 100% hydrogen evolution efficiency for electrolyte conductivities of 10 and 50 mS cm⁻¹.

Illustrations regarding the voltage drop due to the insertion of a diaphragm and the maximum hydrogen recovery rate for different conductivities can be found in the supplementary material part.

3.4. Specific electrochemical wastewater treatment costs with hydrogen recovery by means of a diaphragm

The specific running costs of a WEC can be calculated by multiplying the energy demand with the specific electricity costs. Figs. 6 and 7 show the specific running costs based on Eq. (6) for varying COD current efficiencies and electrolyte conductivities of 10 and 50 mS cm⁻¹, respectively. The practical specific running costs vary in this case for an overall cell voltage of 5.52 V from 0 to about 205 € m⁻³ for COD concentrations between 0 and 100 kg m⁻³ wastewater. For higher electrolyte conductivities the running costs decrease to 0–110 € m⁻³ wastewater.

4. Discussion

4.1. Specific electrochemical wastewater treatment costs without hydrogen recovery

Figs. 3 and 4 model the running costs for industrial wastewater with electrolyte conductivities of 10 and 50 mS cm⁻¹, respectively. The chosen electrode distance of 2 mm and a current density of 100 mA (cm²)⁻¹ correlates to a typical wastewater electrolysis cell. The concentration of the chemical oxygen demand was selected to represent wastewaters, which are suitable for electrochemical advanced oxidation processes like anodic electrooxidation [14]. The treatment cost depends on the concentration of the chemical oxygen demand of the wastewater and the oxidation efficiency. As the chemical oxygen demand of specific wastewater is normally fixed for a constant industrial process, a high anodic oxidation efficiency of the organics is crucial for an economical treatment. Boron-doped diamond electrodes show superior oxidation efficiencies compared to other electrodes like Ti/SnO_2–Sb_2O_5, Ti/PbO_2, Ti/Pt, IrO_2–Ta_2O_5, and RuO_2–TiO_2 [7,15]. A high oxygen overpotential of about 2.8 V vs. a standard hydrogen electrode (SHE) and a very weak interaction with the produced hydroxyl radicals are discussed to be the reason for that. The theoretical minimal energy consumption of 9.38 Wh $(g_{COD})^{-1}$ will be reached in case of unlimited electrolyte conductivity and high organic concentrations at a cell voltage of 2.8 V. In practice, however a limited electrolyte conductivity and a lack of organics at the anodes surface for low organic concentrations will lead to oxygen evolution, thus reducing the oxidation efficiency and increasing the energy demand. Also, in the vicinity of further reactive ions like Cl^-, SO_4^-, or CO_3^{2-}, the evolution of hydroxyl radicals is superposed with the evolution of other oxidants like free chlorine, $S_2O_8^{2-}$, or HCO_3^-. The oxidation efficiency in this case is thus not only depending on the hydroxyl radical evolution but is rather complex as it depends on the type and the concentration of the present ions. The oxidation efficiency in such a system can either be increased or diminished, compared to an electrolyte without reactive species.

Assuming an overall oxidation efficiency of about 100%, the specific WEC running costs for wastewaters with a COD of 100 kg (m³)⁻¹ and electricity costs of 0.15 € (kWh)⁻¹ is calculated to 255 and 170 € (m³)⁻¹ for electrolyte conductivities of 10 and 50 mS (cm)⁻¹, respectively.

4.2. Theoretical energy-saving potential through hydrogen recovery

The specific treatment costs can be diminished by hydrogen recovery. Fig. 5 shows the theoretical energy recovery potential as a function of the overall cell voltage and the

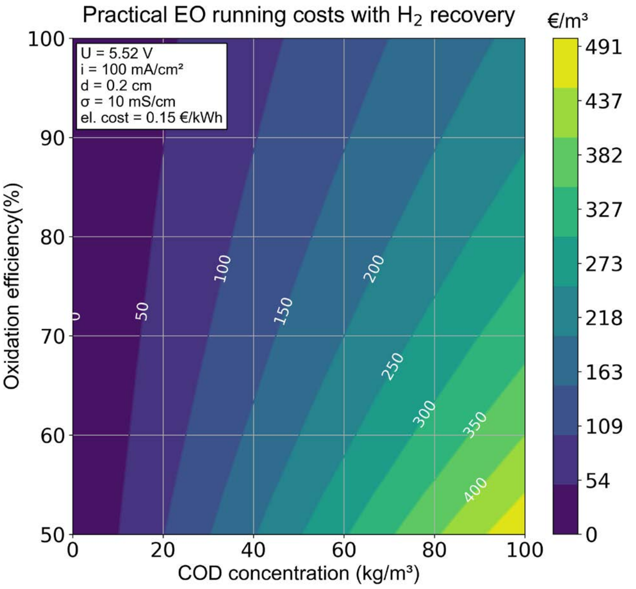

Fig. 6. Specific wastewater treatment costs with hydrogen recovery. Conductivity 10 mS cm⁻¹.

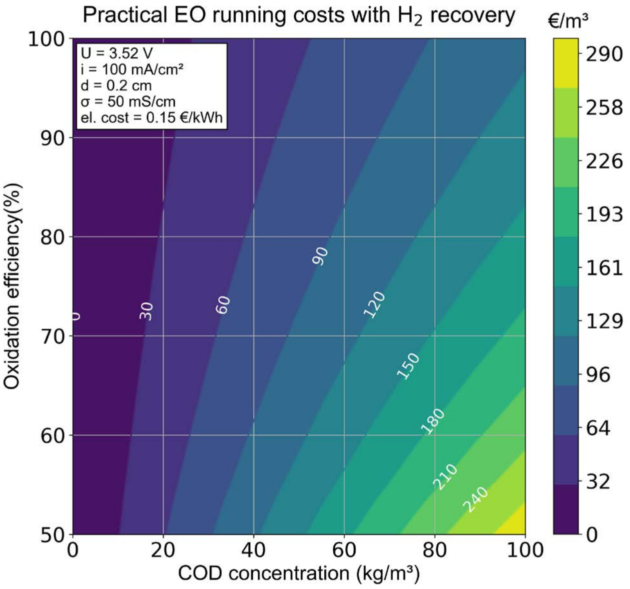

Fig. 7. Specific wastewater treatment costs with hydrogen recovery. Conductivity 50 mS cm⁻¹.

hydrogen evolution reaction efficiency. In the absence of scavenger ions, only water will be reduced on the cathode leading to an ideal hydrogen evolution rate. In the presence of scavengers, however, the hydrogen evolution efficiency can be affected, as some of the ions will be reduced at the cathode, leading to a decrease of the hydrogen production. In the presence of active species and sufficient organic compounds, the hydrogen efficiency may however show no diminished values compared to pure water reduction at the cathode. The theoretical energy recovery potential as calculated in this publication does not consider any additional losses, for example, the *in-situ* separation of the hydrogen by means of a diaphragm or the conversion efficiency of a downstream fuel cell to generate electricity from hydrogen. The practical energy recovery rate will therefore be lower than the proposed theoretical one. As the energy demand for the wastewater electrolysis cells rises with increasing cell potential, but the energy recovery through hydrogen according to Eq. (5) is independent of the cell potential, the proportion of energy recovery is higher for low cell potentials. At cell potentials of 8 V only 8%–16% of the total energy can be theoretically recovered, whereas at a cell potential of 4 V already 16%–32% of the initial energy can be saved. Assuming an infinitive electrolyte conductivity, the ohmic losses of the cell will be zero and the cell voltage equals the reversible cell potential, which in this case is about 2.8 V, representing the sum of the individual potentials to (a) reduce protons or water at the cathode and (b) the potential to produce hydroxyl radicals at the anode. If in addition to that, the hydrogen reaction evolution is 100%, which means that no competing reactions happen at the cathode and the cathode also shows no inherent losses in regards to the hydrogen evolution, the theoretical energy recovery through hydrogen is at a maximum. In this case, Eq. (7) equals $E_{(\text{WEC–H\_(2,theoretical)})} = (0.42\text{ L H}_2 \times \text{Ah}^{-1} \times 2{,}995\text{ Wh} \times \text{Ah}^{-1})/2.8\text{ V} \times 100 = 45\%$. Under this theoretical condition, 45% of the energy applied to the cell can be recovered.

4.3. Effects of a separator on the theoretical energy savings through hydrogen recovery

Evolving hydrogen can be used in a downstream fuel cell to recover a proportion of the energy required for the electrochemical treatment of the wastewater. However, the requirements for the purity of the hydrogen are challenging. Depending on the type of fuel cell, chlorine and carbon monoxide might lead to poisoning. Hydrogen therefore has to be separated prior to the fuel cell application. Ideally, this is done by dividing the wastewater electrochemical cell using a diaphragm. Diaphragms are separators based on electrically insulating and highly porous materials. The main function of diaphragms is to prevent mixing of the evolving gases at the cathode and anode. Diaphragms also should hinder convection and diffusion of charged and uncharged compounds and at the same time allow the migration of charge carriers between the electrodes. In order to minimize the additional electrical resistance caused by the diaphragm, the separator should allow to be soaked by the electrolyte [16]. Typical materials for separators are polyethylen, microporpus polyvinylchloride, or various non-woven fabrics. The implementation of a diaphragm will introduce an additional electrical resistance leading to a reduction of energy savings through hydrogen recovery. The additional electrical resistance consists, as shown in Eq. (9), of the specific electrical resistance of the diaphragm itself and of the increasing electrode distance through the thickness of the diaphragm. Table 1 shows a list of typically used separators in water electrolysis as well as their specific properties.

The thickness of the diaphragms shown in Table 1 varies between 0.26 and 0.5 mm. The implementation of the diaphragm between the electrodes will lead to an increased electrode distance. Depending on the applied current density and the conductivity of the electrolyte, a specific voltage drop over the thickness of the diaphragm will occur, leading to a reduced energy recovery rate. At a current density of 200 mA $(\text{cm}^2)^{-1}$ an additional electrode distance of 1 mm will already lead to an increase of 400 mV–2 V for electrolyte conductivities of 10 and 50 mS cm^{-1}, respectively. Next to the voltage drop due to the increased electrode distance, the specific electrical resistance inherent to the diaphragm material will further add to the voltage drop over the diaphragm. However, the voltage drop is far less as it is due to a higher electrode distance. The voltage drop due to the specific resistance depends only on the applied current density and lies below 100 mV for specific resistances of up to 500 mΩ cm^2 and current densities up to 200 mA $(\text{cm}^2)^{-1}$, thus accounting only for a small proportion of the total voltage drop caused by the diaphragm.

The implementation of a diaphragm leads to a diminishing of the theoretical energy-saving potential through hydrogen recovery. Depending on the conductivity of the electrolyte, the effects of the electrical resistance of the separator are more or less visible. An electrolyte conductivity of 10 mS cm^{-1} leads at a cell voltage of 5 V and at a hydrogen evolution reaction efficiency of 100% to an energy recovery reduction compared to the theoretical value of 2.4%, whereas it is only 0.6% at an electrolyte conductivity of 50 mS cm^{-1}.

4.4. Specific electrochemical wastewater treatment costs with hydrogen recovery by means of a diaphragm

Figs. 6 and 7 show the reduction of the specific wastewater treatment costs when hydrogen is recovered. The reduction of energy costs is increasing with falling cell potentials. At higher cell potentials, hydrogen recovery only accounts for a small proportion of the overall energy demand, and energy savings are almost negligible. Assuming an overall oxidation efficiency and hydrogen evolution rate of 100%, the specific wastewater running costs for wastewaters with a COD of 100 kg $(\text{m}^3)^{-1}$ is calculated to 110 and 205 € $(\text{m}^3)^{-1}$ for cell voltages of 3.52 and 5.52 V, respectively. This amounts to a treatment cost reduction of 36% and 20%, respectively.

4.5. Comparison of the running costs to alternative disposal methods

Fig. 8 shows a comparison of the running costs of a WEC system with and without hydrogen recovery to alternative waste disposal methods. The disposal costs were inquired from a local waste management company in Bavaria and

Table 1
List of different diaphragms used for acidic and alkaline batteries

Trade name	Manufacturer	Material	Thickness (mm)	Specific resistance (mΩ × cm²)	Application medium
DARAMIC industrial CL	Daramic Global Headquarters 11430 N. Community House Rd., Suite 350 Charlotte, NC 28277 USA	Polyethylene	0.5	240	Acidic
AMER-SIL HP	AMER-SIL S.A. Luxembourg, 61, rue d'Olm, 8281 Kehlen, Luxembourg	Microporous PVC	0.5	150	Acidic
Gesintertes PVC	Separatorenerzeugung GmbH Jungfer PE u. PVC Separatoren, Dr. Leopold Jungferstraße, 9181 Feistritz/Rosental, Austria	Sintered PVC	0.5	300	Acidic
Viledon FS 2183	Freudenberg Filtration Technologies, Höhnerweg 2, 69469 Weinheim	PVA-fleece	0.33	40	Alkaline
Viledon FS 2117	Freudenberg Filtration Technologies, Höhnerweg 2, 69469 Weinheim	PA-fleece	0.33	40	Alkaline
Viledon FS 2123 WI	Freudenberg Filtration Technologies, Höhnerweg 2, 69469 Weinheim	PE/PP-fleece	0.26	70	Alkaline

will apply to Germany, but may vary for other countries. It can be seen, that under the assumptions made in this paper and electricity costs of 0.15 € kWh^{-1}, the running costs for the WEC system lie within the range of chemical–physical treatment costs for low cell voltages. Incineration with specific costs between 490 and 665 € t^{-1} is under those assumptions more expensive. It has to be stated, that the shown costs of the WEC system only cover the running costs, investment, and maintenance costs for the system itself are not considered. Fig. 8 also shows clearly, that the recovery of hydrogen is an effective method to further reduce the running costs of a WEC system and that the proportion of energy recovery is higher with lower cell voltage. At a cell potential of about 3.5 V almost 33% of the energy can be recovered, whereas at a cell potential of 8 V only a very small proportion of about 3% can be regained.

5. Conclusion

Hydrogen recovery in wastewater electrolysis cells leads to a reduction of the overall energy input and thus minimizes the specific treatment costs. Parameters to maximize the energy recovery through hydrogen in practical wastewater electrolysis cells are the hydrogen evolution reaction η_{HER}, the oxidation efficiency η_{OX}, the current density j, the electrode distance d, and the specific conductivity Λ of the electrolyte. The electrolyte conductivity has the highest influence on the treatment costs as it governs the cell potential required for a specific current density. Lower cell potentials lead to less specific energy consumption for the anodic oxidation reaction. Furthermore, the energy proportion, which can be recovered via hydrogen recovery with a diaphragm, rises with falling cell potential. At best, about 45% of the energy demand can be theoretically recovered. The electrical resistance and the higher electrode distance through the implementation of the diaphragm leads to a reduction of the theoretical energy recovery rate depending on the electrolyte conductivity, the specific resistance of the diaphragm, and the current density applied. In order to minimize the energy consumption of practical wastewater electrolysis cells, an adjustment of the electrolyte conductivity via acids, alkalis, or conductive salts is recommended. The running costs of a practical WEC system are already lower as the disposal in an incineration plant and can compete with chemical–physical treatment methods. Energy recovery through hydrogen will help to make WEC systems even more economically feasible. In order to verify the simulation results given in this publication, a divided wastewater electrolysis cell will be developed at Fraunhofer UMSICHT. The system will allow a systematic examination of the wastewater purification process and the gas evolution rate.

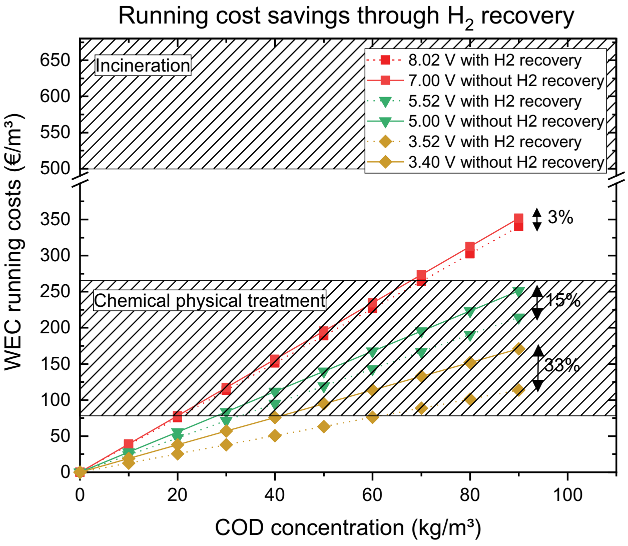

Fig. 8. WEC running costs in comparison with alternative disposal costs.

Acknowledgments

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Symbols

$C_{E(\mathrm{COD})}$ — Specific electricity running costs, € kg $_{\mathrm{COD}}^{-1}$
P_{COD} — Eliminated COD, g O_2
U_{EC} — Voltage necessary to produce Hydroxyl radicals, V
J — Current density, mA $(\mathrm{cm}^2)^{-1}$
D — Electrode distance, cm
Λ — Conductivity, mS cm^{-1}
η_{OX} — Current efficiency for COD removal, %
EC — Electricity cost, € kWh^{-1}
c_{COD} — COD concentration of the wastewater, kg O_2 $(\mathrm{m}^3)^{-1}$
$C_{E(\mathrm{m}^3)}$ — Specific running costs in regards to the COD concentration, € $(\mathrm{m}^3)^{-1}$
$Q_{(\mathrm{COD})}$ — Electrical charge in regards to COD removal, Ah $(\mathrm{m}^3_{\mathrm{wastewater}})^{-1}$
$\ddot{A}_{e\mathrm{H}_2}$ — Faraday equivalent for hydrogen, $\mathrm{g}_{\mathrm{H}_2}$ Ah^{-1}
P — Hydrogen density, g L^{-1}
η_{HER} — Hydrogen evolution reaction efficiency, %
$V^{\bullet}_{\mathrm{H}_2}$ — Volumetric hydrogen production, $\mathrm{m}^3_{\mathrm{H}_2}$
E_{H_2} — Specific energy recovery, kWh
$\mathrm{HHV}_{\mathrm{H}_2}$ — Higher heating value for hydrogen, kWh $(\mathrm{m}^3_{\mathrm{H}_2})^{-1}$
U — Cell voltage, V
$E_{\mathrm{WEC\text{-}H}_{2,\mathrm{theoretical}}}$ — Energy saving through hydrogen recovery, %
R_{Sep} — Electrical resistance separator, Ω cm²
U_{Sep} — Voltage due to separator, V
d_{Sep} — Separator thickness, mm
U_{Sep} — Additional voltage due to separator, V
$E_{\mathrm{WEC\text{-}H}_{2,\mathrm{real}}}$ — Energy savings through hydrogen recovery with consideration of the electrical resistance of the separator, %

References

[1] A. Martínez-Huitle, C. Sergio Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, Chem. Soc. Rev., 35 (2006) 1324–1340.

[2] S. Garcia-Segura, J.D. Ocon, M.N. Chong, Electrochemical oxidation remediation of real wastewater effluents – a review, Process Saf. Environ. Prot., 113 (2018) 48–67.

[3] K. Cho, M.R. Hoffmann, Molecular hydrogen production from wastewater electrolysis cell with multi-junction $\mathrm{BiO}_x/\mathrm{TiO}_2$ anode and stainless steel cathode: current and energy efficiency, Appl. Catal., B, 202 (2017) 671–682.

[4] W. Ma, Z. Cheng, Z. Gao, R. Wang, B. Wang, Q. Sun, Study of hydrogen gas production coupled with phenol electrochemical oxidation degradation at different stages, Chem. Eng. J., 241 (2014) 167–174.

[5] Y. Yang, L. Lin, L.K. Tse, H. Dong, S. Yu, M.R. Hoffmann, Membrane-separated electrochemical latrine wastewater treatment, Environ. Sci. Water Res. Technol., 5 (2019) 51–59.

[6] A. Kapałka, G. Fóti, C. Comninellis, Kinetic modelling of the electrochemical mineralization of organic pollutants for wastewater treatment, J. Appl. Electrochem., 38 (2007) 7–16.

[7] C. Comninellis, G. Chen, Electrochemistry for the Environment, Springer, New York, NY, 2010.

[8] P. Quaino, F. Juarez, E. Santos, W. Schmickler, Volcano plots in hydrogen electrocatalysis - uses and abuses, Beilstein J. Nanotechnol., 5 (2014) 846–854.

[9] C. Comninellis, A. Nerini, Anodic oxidation of phenol in the presence of NaCl for wastewater treatment, J. Appl. Electrochem., 25 (1995) 23–28.

[10] S. Kim, S.K. Choi, B.Y. Yoon, S.K. Lim, H. Park, Effects of electrolyte on the electrocatalytic activities of RuO_2/Ti and Sb–SnO_2/Ti anodes for water treatment, Appl. Catal., B, 97 (2010) 135–141.

[11] H. Park, C.D. Vecitis, M.R. Hoffmann, Electrochemical water splitting coupled with organic compound oxidation: the role of active chlorine species, J. Phys. Chem. C, 113 (2009) 7935–7945.

[12] J. Kim, D. Kwon, K. Kim, M.R. Hoffmann, Electrochemical production of hydrogen coupled with the oxidation of arsenite, Environ. Sci. Technol., 48 (2014) 2059–2066.

[13] A. Kraft, M. Stadelmann, M. Blaschke, Anodic oxidation with doped diamond electrodes: a new advanced oxidation process, J. Hazard. Mater., 103 (2003) 247–261.

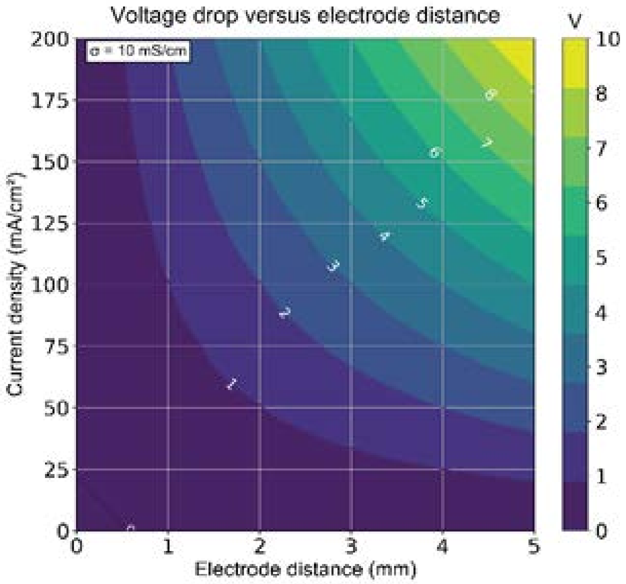
[14] Y. Nishiki, Anodic Decomposition of Toxic Compounds (Anodic Mineralization), G. Kreysa, K.-i. Ota, R.F. Savinell, Eds., Encyclopedia of Applied Electrochemistry, Bd109, Springer New York, New York, NY, 2014, pp. 78–85.

[15] C.A. Martínez-Huitle, M. Panizza, Electrochemical oxidation of organic pollutants for wastewater treatment, Curr. Opin. Electrochem., 11 (2018) 62–71.

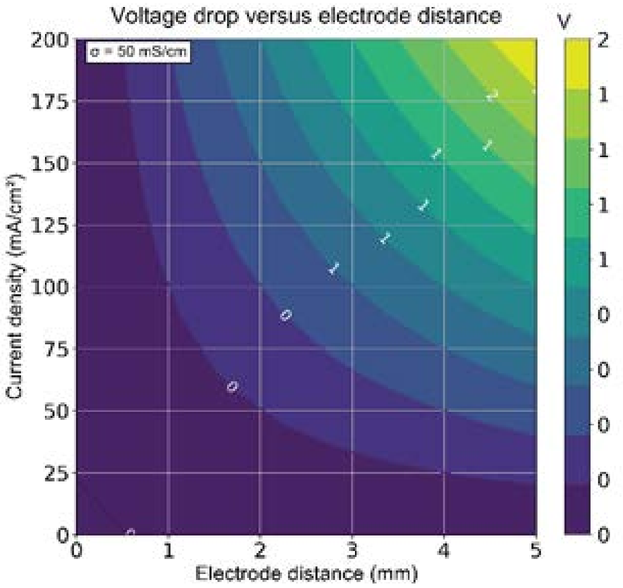
[16] V.M. Schmidt, Elektrochemische Verfahrenstechnik: Grundlagen, Reaktionstechnik, Prozeßoptimierung, Wiley-VCH, Weinheim, 2004.

Supplementary information

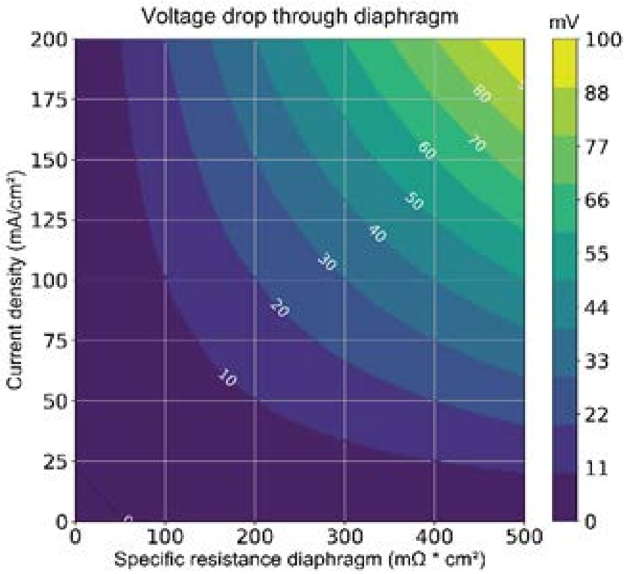
Effects of a diaphragm on the theoretical energy savings through hydrogen recovery



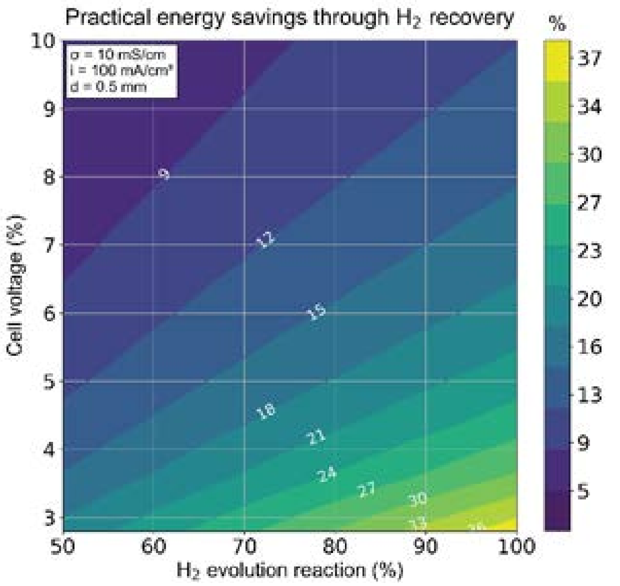
Additional voltage drop as a function of current density and electrode distance, Conductivity: 10 mS cm^{-1}.



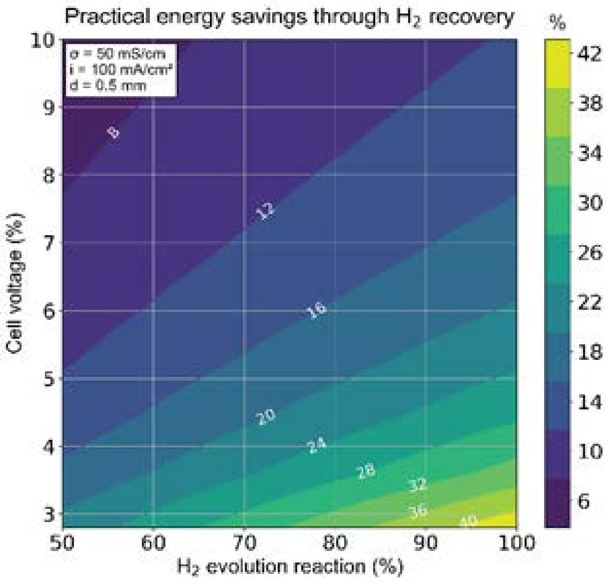
Additional voltage drop as a function of current density and electrode distance, Conductivity: 50 mS cm^{-1}.



Additional voltage drop as a function of current density and the specific electrical resistance of the diaphragm.



Energy recovery potential by means of a separator as a function of the cell voltage and the hydrogen evolution rate.



Energy recovery potential by means of a separator as a function of the cell voltage and the hydrogen evolution rate.