Electrolyzer Dynamics Project, FM1015 Modelling of Dynamic Systems

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- rev Sept 29, 2025: minor added precision in Section 3.3.6 + two added data in Table 5

- rev Sept 30, 2025: corrected sign of log H in Section 3.3.6

- rev Oct 10, 2025: corrected expression for $\frac{1}{T}$ in Section 3.3.6. Added $T_c^{H_2O}$ in Table 5 of Appendix A. Corrected the row on $\dot{m}_p^{c,r,ref}$ in Table 6 of Appendix A

Contents

1. Introduction

1.1. General instructions

- This project is a *work requirement* in course FM1015 Modelling of Dynamic Systems:

  - Contributing in the project and the project report is a *work requirement*, and a 50% score is required for the project report to pass this work requirement.

  - Contributing in an oral presentation of the group project is a *work requirement*, and good presentation and understanding of the project report is a requirement to pass the work requirement.

  - The project problem will constitute the *core* of the individual multiple-choice exam ca. December X, 2025.[1]

- The group:

  - You are expected to work in a group 3–5 students. You should find group members yourselves and then inform me about who are in your group.

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[1]There may be exam questions unrelated to the project problem. If so, these will constitute a minor part of the exam.

- You are recommended to form groups with a mixture of background (EPE, ITA, PEET; different nationalities, etc.) — this will give the group a good variation in process knowledge, control engineering, electrical engineering, programming, and communication practice.

- Those who have not established groups by Friday September 12, 2025, will be placed in groups by me.

- Do *not* establish a Canvas "Student Group" folder yourself — instead, send a message to the lecturer using the *Canvas Inbox* messaging system, where you state who will be group members, and then the lecturer will establish a *Canvas Project Group folder*.[2]

- The report:
  - The *group* is expected to write and submit a single group report in a *Canvas Project Group folder*.

  - A mid-way, partial report should be submitted in the Canvas Project Group folder by Friday, October 17, 2025 at 16:00. In this partial report, a dynamic model with first simulation results should be included.

  - A single document final report, PDF format, maximum of 15 pages + a single cover page, is to be submitted in the Canvas group folder by Friday, November 7, 2025 at 23:59.[3]

- The oral project presentation:
  - Each group has 7 minutes *in total* for a presentation (PowerPoint, etc.), and every group member needs to present something. Thus, 1–2 minutes per group member.

  - In preparing the presentation: *remember who the audience is*. The audience is I, the lecturer, who created the group project. Do not waste time by (i) including figures from the task description, (ii) including equations from the task description: I know these figures and equations, so there is no need to repeat them. Instead, focus on what you have done in the project — remember you have only 7 minutes available to present your work and results.

  - Directly following the presentation will be a brief examination of the work, where every group member will be asked at least one question. In total, 15 minutes will be allotted to each group (switching group + presentation + questions).

  - *Campus students* will give the presentation in class on Friday November 14, 2025, starting 10:15 until finish; *industry master students* and on-line students *who can be present*, are recommended to present in class on this day.

  - *On-line students* and *industry master* students who *can not be present*, will give their presentation via MS Teams at a different time — *individual appointments* for Teams presentations will be set up with the lecturer. These presentations

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[2]*Reason*: A "Student Group" established by students allows a student to be member in multiple Student Groups, and it is impossible to keep track of whether the student is in a project group or not. The lecturer can establish a type of "Project Group" where students can only be member of one such Project Group.

[3]Yes, maximum 15+1 pages. *Not a single page extra* for computer code, plots, etc.

should be given *before* November 14, 2025: (i) I need to inform the exam office about who failed in the project and thus can not participate in the exam at least 2 weeks prior to the exam, and (ii) I do not want to delay the publication in Canvas of the lecturer's project solution — this solution is useful for exam preparation.

The notation used in this project more or less follows the standard notation in the course. This notation may vary from the notation used in the actual problem field.

1.2. Background

United Nations (UN) has made Affordable and Clean Energy one of 17 goals for Sustainable Development[4]. Affordable energy is a key factor in development of societies, and is therefore key in giving equal opportunity to all people.

One possible source of energy is energy in solar irradiation, which can be converted to electricity via solar panels/photo voltaic (PV) panels. Another possible source is energy in wind, which is converted to mechanical energy via wind turbines, and then to electricity via an electric generator.

Both solar and wind energy is *intermittent* in their nature: they have a somewhat random nature, production of energy from them can not be controlled to when the energy is needed. To get around this problem of intermittency, it is necessary to be able to store wind and solar energy when when the production exceeds what is needed, and to be able to take energy from this storage when the production is less than what is needed.

Electricity can be stored *electrically* in batteries, superconductors, etc. Electricity can be stored mechanically by pumping water up into elevated reservoirs. A third possibility is to convert electricity to gas via electrolysis of water; the result is hydrogen which can be stored or converted to other gases (e.g., ammonia) for storage. When we need more electricity than what is produced by solar or wind power (e.g., in the night), we can convert gas back to electricity via fuel cells.

Batteries, electrolyzers, and fuel cells are all *electrochemical* processes, which combine electrical engineering processes with chemical engineering processes. In this project, the focus is on *electrolysis of water* into hydrogen (and oxygen).[5]

1.3. Project aim

This project is designed to give experience in formulating and solving dynamic models of systems, and thus to aid in the learning of the content of course FM1015. Furthermore, the purpose of the project and the presentation is to give the students experience in group work and communication of findings. Because the final exam will be based on the project work, active project participation helps prepare for the final exam.

More specifically, in this group project, models of electrolysis cells and an electrolysis stack for converting water into hydrogen and oxygen will be considered. Electrical engineering is not part of the course syllabus, thus if electric models are needed, these will be provided in this project text. A dynamic model of an electrolysis stack includes material balances for the gases, as well as a model of water balance, and energy balance for consideration of the temperature. To simplify the model, we will assume perfect control of the stack temperature.

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[4]https://sdgs.un.org/goals
[5]In the 2023 project, the focus was on fuel cells.

A first step in the project is to get familiar with electrolysis cells and electrolysis cell operation (Section 2), as well as a electrolysis stack and surrounding equipment (Section 3). A *second step* involves finding steady state amounts of material in separator volumes and steady flows. A *third step* involves developing the complete model of a fuel cell stack, and carrying out experiments on the model. A *final step* is to write a short report where you focus on your *findings*, and do not repeat text from the task description.

At the end of this project, you will be able to:

1. Understand the basic principles of developing electrolysis cell models and electrolysis stack models for Hydrogen production,

2. Solve the model using a computer tool (OpenModelica, Python, Julia, MATLAB, etc.),

3. Analyze the system behavior through experiments on the model, and

4. Understand safety aspects related to water electrolysis.

2. Electrolyzer Cells

2.1. Basic concepts

An *ion* (from Greek: "to go")[6] is an electrically charged particle that moves/"goes" when positioned in an electrical field. Ions are named as follows:

Anion: A negatively charged ion,

Cation: A positively charged ion,

see Fig. 1.

An electrochemical cell has both electrical and chemical characteristics. The electrochemical cell consists of two *electrodes*, which are solid metals of different types (e.g., copper, silver, brass, etc. for one electrode; zinc, tin, etc. for the other), separated by an *electrolyte* which is a liquid or solid material with ions that are free to move — historically, the first electrolyte was a spongy material soaked in brine (salt water). The electrodes are denoted anode and cathode:

Anode: *Anions* move toward the electrode denoted the *anode*, while

Cathode: *Cations* move toward the electrode denoted *cathode*.

This implies that what is anode and cathode, depends on the operation of the electrochemical cell, see Fig. 1. The electrolyte contains some separation/membrane mechanism that blocks the movement of reactants/electrons/etc. through the electrolyte, and only allows for the passage of certain ions through the electrolyte.

Electrochemical *reactions* take place at the *interface* between a reactant (gas or liquid), an electrode, and the electrolyte, in what is known as the "three-phase boundary" or "triple-point junction". The reaction rates at the triple-point junction can be varied by either (i) increasing the surface/contact area — which is done by making the electrode

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[6]Coined in 1834 by Michael Faraday after suggestion by linguist Rev. William Whewell.
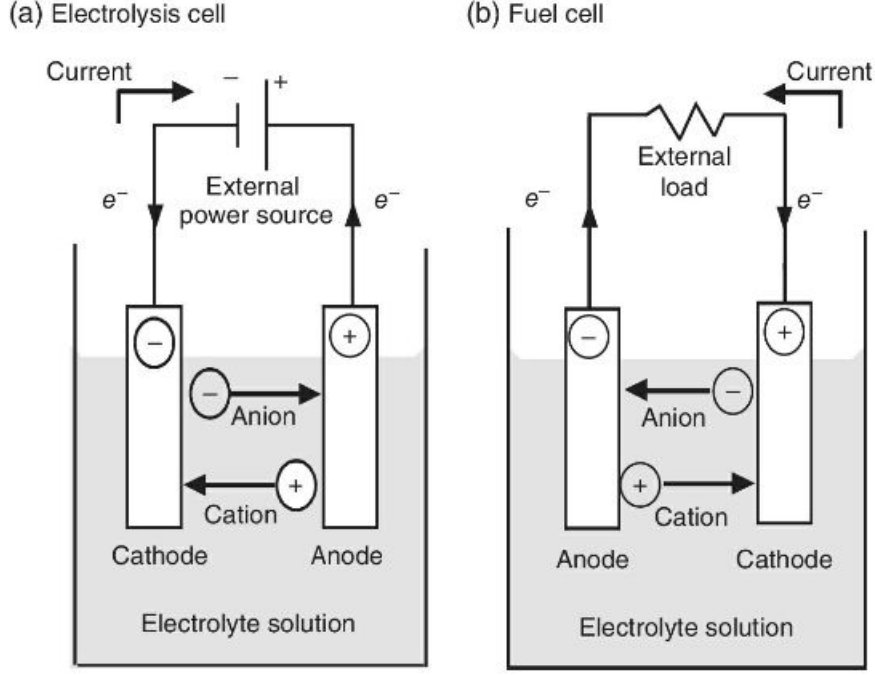
Figure 1: Terminology employed in operation of (a) Electrolysis cells, and (b) Fuel cells. From Dicks & Rand (2018).

porous, (ii) by doping a *catalyst* into the electrode surface, (iii) by operating at a high temperature, or (iv) operating the the system at high pressure.

Each electrode and the adjoined triple-point junction constitutes a *half-cell*; for each of the two half-cells, there is a half-cell reaction involving electrons e⁻ in either an

- *oxidation* reaction (increasing the charge of some ions by releasing electrons), or

- *reduction* (reducing the charge of some ions by taking up electrons).

The half-cell reactions depend both on (a) the overall materials involved, and (b) the electrolyte.

Associated with the electrochemical system is an *external circuit* where negatively charged electrons e⁻ move in an electrically conducting wire; the material of the wire is chosen to allow for free movement of electrons, e.g., copper, silver, or similar. From historic convention, *electric current* i is defined in the opposite direction of the flow of electrons, as in Fig. 1. Let $\dot{n}_{e^-}$ be the molar flow rate of electrons. The electric current i is given as

$$i = -F \cdot \dot{n}_{e^-} \tag{1}$$

where F is Faraday's constant,[7]

$$F = 9.648\,533\,212\,331\,001\,84 \cdot 10^4\,\text{A}/\,(\text{mol/s}) \approx 9.6485 \cdot 10^4\,\text{C/mol}.$$

The prefix "an-" comes from Greek *ano-dos* ("upwards"-"a way"), indicating that the electrons go "upwards" from the anode and into the external electric circuit, Fig. 1.

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[7]In a revision to *Système international d'unités* (SI) in 2019, Avogadro's constant/number N_A was redefined to be exactly $N_A = 6.022\,140\,76 \cdot 10^{23}\,\text{mol}^{-1}$, while the elementary charge q_e was redefined to be exactly $q_e = 1.602\,176\,634 \cdot 10^{-19}\,\text{C}$. The elementary charge is the electric charge of a single proton H^+. Faraday's constant is defined as $F \triangleq N_A \cdot q_e$, and is thus an exact number.
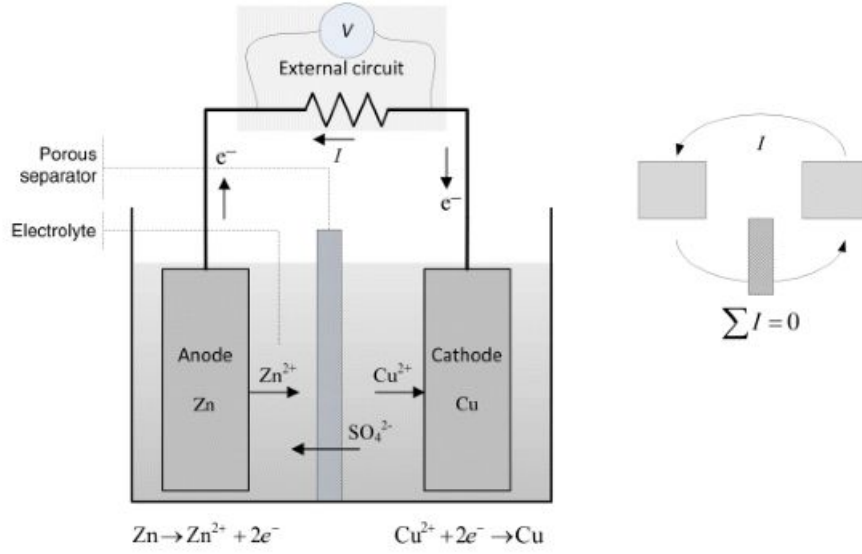
Figure 2: Daniell cell. From Fuller & Harb (2018).

The prefix "cat-" comes from Greek *katho-dos* ("downwards"-"a way") implying that the electrons go "downwards" towards the cathode in the external electric circuit.

2.2. Half-cell and overall reactions

For simplicity, consider a single reaction, e.g.,

$$a_1 A_1 + a_2 A_2 \rightarrow b_1 B_1 + b_2 B_2 \tag{2}$$

$$\Downarrow$$

$$0 \rightarrow \underbrace{\begin{pmatrix} -a_1 & -a_2 & b_1 & b_2 \end{pmatrix}}_{=\nu} \begin{pmatrix} A_1 \\ A_2 \\ B_1 \\ B_2 \end{pmatrix}. \tag{3}$$

More generally, we can write the reaction as

$$0 \xrightarrow{r} \nu S \tag{4}$$

where ν is the stoichiometric matrix (here: vector) with positive sign for the products, S is the vector of species, and r is the rate of reaction.

In the case of multiple reactions, this just results in multiple rows in the stoichiometric matrix ν, and possibly an expansion of the species vector S — in case new species are introduced.

Example 1. Daniell cell

Consider the Daniell cell in Fig. 2, which is an early battery construction.[8]

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[8]https://en.wikipedia.org/wiki/Daniell_cell

The *anode*[9] is made of *zinc*, while the *cathode* (positive electrode) is made of *copper*. The half-cell reaction at the *anode* in Fig. 2 is the *oxidation* reaction

$$Zn \rightarrow Zn^{2+} + 2e^-$$

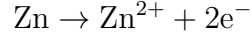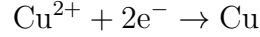where *zinc* reacts to a zinc ion with *increased* charge (hence: oxidation) by releasing 2 electrons. The half-cell reaction at the *cathode* is the *reduction* reaction

$$Cu^{2+} + 2e^- \rightarrow Cu$$

where *copper* is produced when a positively charged copper ion takes up 2 electrons, i.e., the charge is *reduced* (hence: reduction).

Observe that the above half-cell reactions are "overall" half-cell reactions; in reality, the half-cell reactions are more complex.

The zinc ion exists in the electrolyte part surrounding the anode half-cell, while the copper ion exists in electrolyte part surrounding the cathode half-cell. Observe that both the zinc and copper ions are positively charged; both are *cations*. The positively charged ions (cations) move towards the cathode, hence the copper electrode is the cathode.

Because it is necessary to have overall electron-neutrality in the electrolyte, there must be an accompanying *negatively* charged ion, the *anion*. In the electrolyte depicted in Fig. 2, the anion is sulfate, SO_4^{2-}. To this end, the electrolyte associated with the anode part is disassociated zinc sulfate, $ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$, while the electrolyte associated with the cathode part is copper sulfate, $CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$. The negatively charged ions (anions) move towards the anode, which is the zinc electrode.

The overall cell reaction is found by summing the two half-cell reaction so that charge is balanced. To achieve charge balance, it is necessary to *scale* each of the half reactions so that the electron has the same coefficient associated to it in both half reactions, for example, scaling the half reaction so that each half reaction involves *one* electron:

$$\frac{1}{2} \cdot \left(Zn - Zn^{2+} - 2e^-\right) \rightarrow \frac{1}{2} \cdot \left(Cu - Cu^{2+} - 2e^-\right)$$

$$\Downarrow$$

$$\frac{1}{2}Zn + \frac{1}{2}Cu^{2+} \rightarrow \frac{1}{2}Zn^{2+} + \frac{1}{2}Cu + \underbrace{1}_{=\nu_{e^-}^{(1)}} \cdot \left(e^- - e^-\right)$$

$$\Downarrow$$

$$\frac{1}{2}Zn + \frac{1}{2}Cu^{2+} \rightarrow \frac{1}{2}Zn^{2+} + \frac{1}{2}Cu.$$

With Cu as product and species vector $S = (Zn, Cu^{2+}, Zn^{2+}, Cu)$, the stoichiometric "matrix" is

$$\nu^{(1)} = \left(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right).$$

Observe in particular:

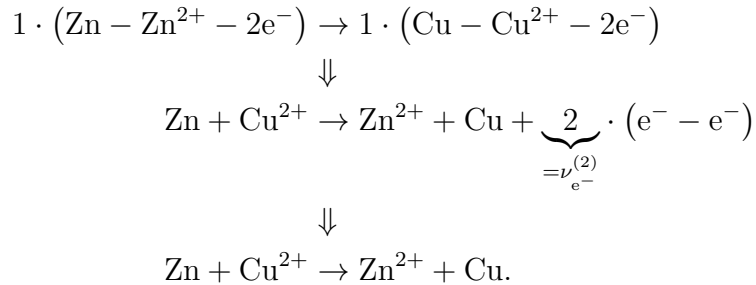1. In the overall cell reaction, the electrons e^- cancel out. This is necessary in order to conserve charge. Next,

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[9]In a *discharging* battery, the *anode* is the negative electrode because electrons go up from the anode into the external circuit, which implies that the current goes in the opposite direction — requiring that the cathode has higher potential (i.e., is positive) compared to the anode.

2. In the overall cell reaction, at least one substance is uniquely present at each of the electrodes, and

3. With the given scaling of the half reactions, there is a (hidden) stoichiometric coefficient of $\nu_{e^-}^{(1)} = 1$ for the electron, and

4. A "normalized" stoichiometric matrix $\nu \triangleq \nu^{(1)}/\nu_{e^-}^{(1)}$ is

$$\nu = \left(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right).$$

In reality, it is not necessary to scale the half reactions so that each half reaction involves one electron. A more common scaling would be to have coefficient unity in as many terms as possible in the *overall* reaction. Thus, the following would be more common:

$$1 \cdot \left(\mathrm{Zn} - \mathrm{Zn}^{2+} - 2\mathrm{e}^- \right) \rightarrow 1 \cdot \left(\mathrm{Cu} - \mathrm{Cu}^{2+} - 2\mathrm{e}^- \right)$$
$$\Downarrow$$
$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu} + \underbrace{2}_{=\nu_{e^-}^{(2)}} \cdot \left(\mathrm{e}^- - \mathrm{e}^- \right)$$
$$\Downarrow$$
$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}.$$

With the same species vector as above, the stoichiometric vector for the overall reaction is now

$$\nu^{(2)} = (-1, -1, 1, 1).$$

This time, with the given scaling of the half reactions, the (hidden) stoichiometric coefficient for the electron is $\nu_{e^-}^{(2)} = 2$.

Remark 1. Stoichiometric invariance

A first *key observation* is that

$$\nu^{(2)}/\nu_{e^-}^{(2)} = \left(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right),$$

in other words, we see that $\nu^{(j)}/\nu_{e^-}^{(j)}$ is invariant wrt. the scaling of half-reactions. ▲

Remark 2. Need for membrane

A second *key observation* is that the electrolyte must hold a mechanism/barrier/membrane that allows the shared ion in the electrolyte (here: sulfate) to move between the electrodes, while blocking the transport of all other elements (i.e., the other ions — Cu^{2+}, Zn^{2+}, e^-, etc.) between the electrodes through the electrolyte. ▲
As indicated in Fig. 2, the ion that moves between the electrodes in the Daniell Cell is sulfate (SO_4^{2-}), which is a species that does not participate in the half-cell reactions.▲

Example 2. Daniell cell — alternative electrolyte

Consider the following modification of the Daniell cell in Fig. 2: the anode half-cell zinc reaction (oxidation) is as before, but the cathode half-cell reaction changes to the following reaction involving oxygen (instead of the copper electrode),

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O.$$
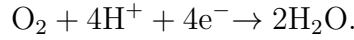
The overall reaction now becomes

$$2 \cdot \left(Zn - Zn^{2+} - 2e^-\right) \rightarrow 1 \cdot \left(2H_2O - O_2 - 4H^+ - 4e^-\right)$$
$$\Downarrow$$
$$2Zn + O_2 + 4H^+ \rightarrow 2Zn^{2+} + 2H_2O + \underbrace{4}_{=\nu_{e^-}^{(1)}} \cdot \left(e^- - e^-\right).$$
$$\Downarrow$$
$$2Zn + O_2 + 4H^+ \rightarrow 2Zn^{2+} + 2H_2O.$$

Here, we assume that water is the product, and define the species vector as $S = (Zn, O_2, H^+, Zn^{2+}, H_2O)$, with stoichiometric vector

$$\nu^{(1)} = (-2, -1, -4, 2, 2).$$

Observe that we needed to multiply the anode reaction (zinc) with 2 to be able to balance out the electrons e^-. Thus, the (hidden) stoichiometric coefficient for the electron is $\nu_{e^-}^{(1)} = 4$.

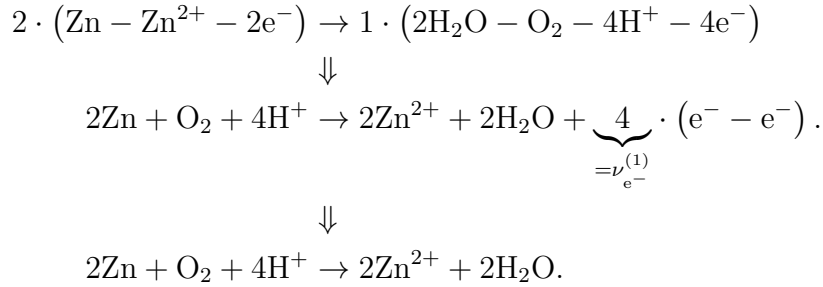Note that, again, it is possible to scale the half-cell reactions differently so that $\nu_{e^-}^{(j)}$ differs from 4. Again, we will find that $\nu^{(j)}/\nu_{e^-}^{(j)}$ is invariant wrt. such scaling;

$$\nu^{(1)}/\nu_{e^-}^{(1)} = \left(-\frac{1}{2}, -\frac{1}{4}, -1, \frac{1}{2}, \frac{1}{2}\right)$$

Also for this case, the shared ion in the electrolyte is sulfate. The cathode side electrolyte consists of disassociated hydrogen sulfate, $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$.[10] ▲

2.3. Electrolyzer with H_2 and O_2 products

Electrolysis cells use electric power to drive chemical reactions where a fuel is split into reactants, Fig. 3.

For electrolysis, the oxidation reaction takes place at the anode, while the reduction reaction takes place at the cathode. As indicated in Fig. 3, *electrons* move out of the anode and towards the cathode, which implies that *electric current* goes the *opposite* way: from the cathode to the anode. This also implies that the anode is connected to the positive external voltage, while the cathode is connected to the negative external voltage. In order to separate the products (oxidized and reduced species), the electrodes are in practice separated by a membrane holding an electrolyte. Figure 4 illustrates water electrolysis.

In water electrolysis, electric power is used to drive the overall reaction

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2. \tag{5}$$

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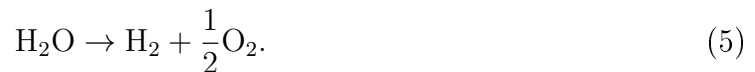
[10]In fact, hydrogen sulfate = sulfuric acid was the original cathode side electrolyte for the Daniell Cell, https://en.wikipedia.org/wiki/Daniell_cell

Figure 3: Principle of electrolysis. From Cavaliere (2023).

Figure 4: Principle of water electrolysis with acidic membrane.

The half-cell reaction producing hydrogen is known as the Hydrogen Evolution Reaction (HER), while the half-cell reaction producing oxygen is known as the Oxygen Evolution Reaction (OER).

Example 3. Acidic electrolyte

In the case of an *acidic* electrolyte/membrane, the overall half-cell reactions are the anode (oxidation reaction, OER)

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \tag{6}$$
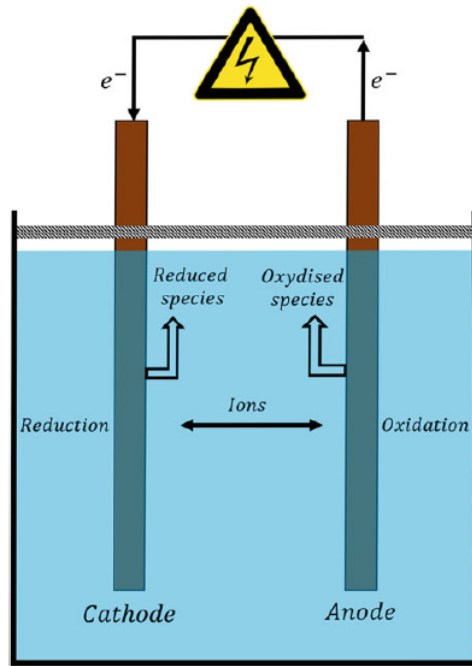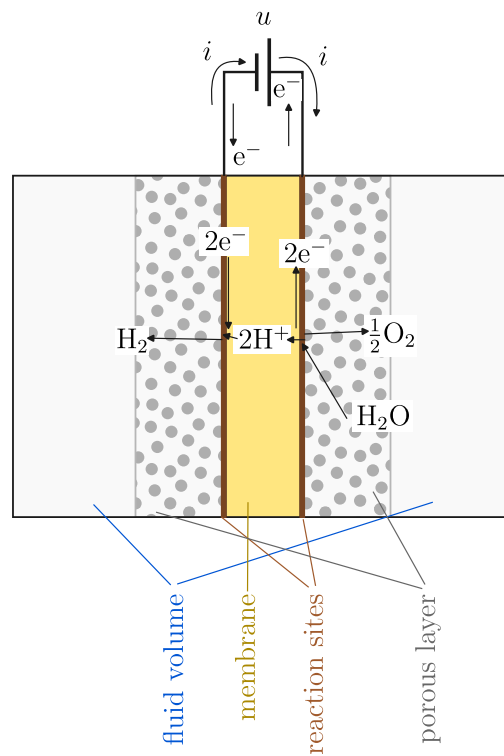
and the overall half-cell reaction at the cathode (reduction reaction, HER)

$$2H^+ + 2e^- \rightarrow H_2. \tag{7}$$

This implies that oxygen is produced at the anode and hydrogen at the cathode. Proton (H^+) moves through the membrane, and water is consumed at the anode. Therefore, when using an acidic electrolyte, water must be available on the anode side.

Remark 3. Supply of water

Norwegian water electrolyzer producer Hystar[11] appears to supply water to the cathode side. Since Hystar uses an acidic electrolyte (PEM), this means that their design must allow for water to diffuse through the membrane and become available on the anode side.[12] ▲

Combining the two half-cell reactions, proceed as follows: take the oxidation reaction and move all terms to the LHS[13] of the arrow, and take the reduction reaction and move all terms to the RHS[14] of the arrow. Adding the expressions, we get

$$1 \cdot \left(H_2O - \frac{1}{2}O_2 - 2H^+ - 2e^- \right) \rightarrow 1 \cdot \left(H_2 - 2H^+ - 2e^- \right)$$

$$\Downarrow$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 + \underbrace{2}_{\nu_{e^-}=2} \cdot \left(e^- - e^- \right) + 2 \cdot \left(H^+ - H^+ \right)$$

$$\Downarrow$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2.$$

Considering hydrogen and oxygen as products, and with species vector $S = (H_2O, H_2, O_2)$, we find stoichiometric vector/matrix $\nu^{(1)}$ and (hidden) electron stoichiometric coefficient ν_{e^-} to be

$$\nu^{(1)} = \begin{pmatrix} -1 & 1 & \frac{1}{2} \end{pmatrix}$$
$$\nu_{e^-} = 2$$

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[11]https://hystar.com/

[12]In fact, hydrogen sulfate = sulfuric acid was the original cathode side electrolyte for the Daniell Cell, https://en.wikipedia.org/wiki/Daniell_cell
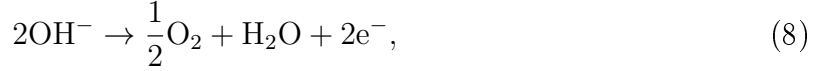
[13]Left Hand Side

[14]Right Hand Side

with scaled stoichiometric matrix

$$\frac{\nu^{(1)}}{\nu_{e^-}} = \left(-\frac{1}{2}, \frac{1}{2}, \frac{1}{4}\right)$$

— which is invariant wrt. choice of coefficients in the overall reactions. ▲

Example 4. Alkaline electrolyte

For alkaline electrolyte/membrane, the overall half-cell reaction for the anode (oxidation reaction, OER) is

$$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-, \tag{8}$$

and for the cathode (reduction reaction, HER),

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-. \tag{9}$$

Again, oxygen is produced at the anode and hydrogen is produced at the anode. This time, hydroxide (OH^-) moves through the membrane, and water is only consumed at the cathode, while water is produced at the anode. Therefore, when using an alkaline electrolyte, water must be available on the cathode side.

Combining the half-reactions in the same manner as for the acidic reaction, we find

$$1 \cdot \left(2OH^- - \frac{1}{2}O_2 - H_2O - 2e^-\right) \rightarrow 1 \cdot \left(H_2 + 2OH^- - 2H_2O - 2e^-\right)$$

$$\Downarrow$$

$$(-1+2) \cdot H_2O \rightarrow H_2 + \frac{1}{2}O_2 + \underbrace{2}_{\nu_{e^-}=2} \cdot \left(e^- - e^-\right) + 2 \cdot \left(OH^- - OH^-\right)$$

$$\Downarrow$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2.$$

Again, considering hydrogen and oxygen as products, and with species vector $S = (H_2O, H_2, O_2)$, we find stoichiometric vector/matrix $\nu^{(1)}$ and (hidden) electron stoichiometric coefficient ν_{e^-} to be

$$\nu^{(1)} = \left(\begin{array}{ccc} -1 & 1 & \frac{1}{2} \end{array}\right)$$
$$\nu_{e^-} = 2$$

with scaled stoichiometric matrix

$$\frac{\nu^{(1)}}{\nu_{e^-}} = \left(-\frac{1}{2}, \frac{1}{2}, \frac{1}{4}\right).$$

In other words: the scaled stoichiometric matrix is invariant wrt. electrolyte, etc. ▲

The real reaction taking place at the electrodes is more complex. The scaled stoichiometric matrix is what matters for *equilibrium* relations, but the real half-cell reactions influences the reactions taking place at *non-equilibrium.*

Alkaline electrolysis (AEL) has a long history (100+ years), while acidic electrolysis in Proton Exchange Membranes (PEM, PEMEL) only has a history of some 25+ years for land-based use. A newer, Anion Exchange Membrane electrolysis (AEMEL) uses an alkaline membrane and attempts to combine the best properties from AEL and PEMEL. Some key properties for these three electrolysis technologies are listed in Table 1.

Table 1: Characteristics of low temperature water electrolysis technologies. Based on Holst et al. (2021).

	AEL	PEMEL	AEMEL
Cathode reaction	HER, Eq. 9	HER, Eq. 7	HER, Eq. 9
Anode reaction	OER, Eq. 8	OER, Eq. 6	OER, Eq. 8
Charge carrier	OH^-	H^+	OH^-
Electrolyte	Liquid electrolyte KOH	Acidic polymer membrane	Polymer membrane with diluted KOH
Temperature	60–90 °C	20–80 °C	50–70 °C
Catalyst	Nickel substrates	Noble metals (platinum, iridium)	Platinum and non-platinum
Current density	0.2–0.6 A/cm^2	1.0–2.5 A/cm^2	0.5–1.5 A/cm^2
Pressure	1 atm–30 bar	1 atm–50 bar (350 bar)	1 atm–35 bar
Advantages	- Mature, robust, proven - Large capacity systems today - Possible to use abundant/inexpensive materials	- High power densities - Compact design - Fast cold start-up - Suitable for high pressure - High product purity	- Can use abundant/cheap materials - Compact design - High pressure operation
Disadvantages	- Alkaline liquid challenging for build material - Low power density/large footprint - Product H$_2$ purification needed - Slow cold-start	- Expensive materials required (titanium, platinum, etc.) - Long-term stability needs to be proven	- Low technology readiness level - Limited long-term stability currently
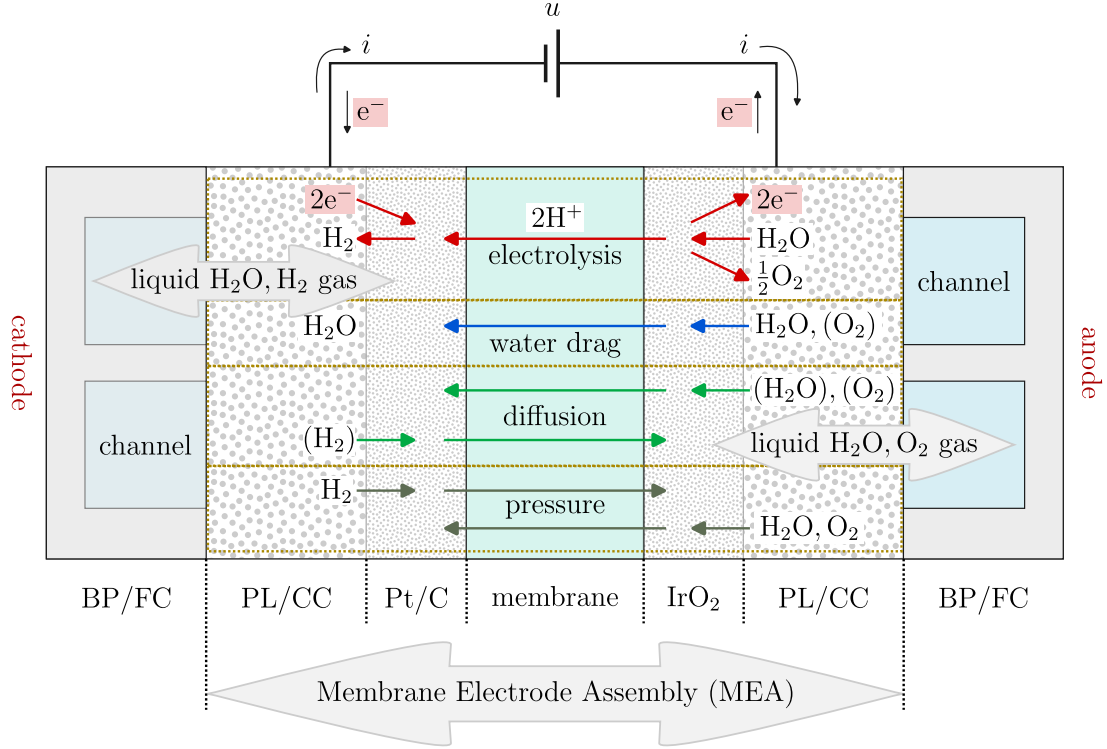
Figure 5: PEM Electrolysis Cell, with (left-to-right) indication of *cathode* side Bipolar Plate with Flow Channel (BP/FL), cathode side Porous Layer/Current Collector (PL/CC), cathode side Catalyst with Platinum on Carbon support (Pt/C). In the middle: solid membrane (Proton Exchange Membrane, PEM). Next, to the left: *anode* side Catalyst with Iridium Oxide catalyst (IrO$_2$), anode side PL/CC, and finally anode side BP/FC. Inspired by Schalenbach et al. (2013), Abdol Rahim et al. (2016), Thampan et al. (2001), Datta et al. (2015).

2.4. Structure of PEM Electrolyzer Cell

In the sequel, Proton Exchange Membrane[15] Electrolyzer (PEMEL) is considered in more detail. PEMEL typically uses pure water as reactant in an overall reaction H$_2$O $\rightarrow$ H$_2$ + $\frac{1}{2}$O$_2$, and is a modern electrolyzer technology. PEMEL is operated at 20–80 °C, requires a system for handling water content, and good temperature control. PEMEL for water is normally operated at as high pressure as possible in the cathode water/hydrogen volume in order to minimize the energy consumption in compressing the product (hydrogen) before storage; typically in the range 30–50 bar. At the same time, the oxygen product is often released to the atmosphere, and it is therefore desirable to operate the anode water/oxygen volume at close to atmospheric pressure. To avoid damaging the membrane with such a high pressure difference across the membrane, some membrane reinforcement is required. An electrolyzer cell is depicted in Fig. 5.

In Fig. 5, purified liquid water is fed to the cell via the anode flow channel, and diffuses through the porous layer (PL/CC) to the catalyst (typically Iridium based, e.g., IrO$_2$) on the electrode. The reaction takes place at the triple point between liquid water, catalyst, and membrane. Produced oxygen (O$_2$) in the electrolysis reaction diffuses back as gas through the porous layer (PL/CC) and into the anode flow channel where it mixes with liquid water, and leaves the electrolysis cell to the water-oxygen separator. Electrons

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[15]Or: Polymer Electrolyte Membrane

(e^-) released in the electrolysis reaction travels via the current collectors (PL/CC) through the external circuit to the cathode side.

Proton (H^+) flows through the membrane from the anode side to the cathode side. Simultaneously, electrons (e^-) enter from the external circuit through the current collectors (PL/CC) and on to the electrodes/catalyst site. The reaction takes place at the triple point between catalyst and membrane, and releases hydrogen gas (H_2).

Protons flowing through the membrane also *drags* liquid (mainly water molecules) along through the membrane (electro-osmotic drag), which causes liquid water to appear on the cathode side where it mixes with the produced hydrogen gas (H_2). It is possible that gases dissolved in the liquid (hydrogen, oxygen) are also dragged with the liquid through the membrane. Water (liquid) and hydrogen (gas) diffuse through the porous layer (PL/CC) and to the cathode side flow channel. Water may or may not be circulated through the cathode flow channel (Fig. 9); water and hydrogen is transported from the cathode flow channel to the water-hydrogen separator.

In addition to water entrained/*dragged* by protons through the membrane, water may also *diffuse* through the membrane — the flow direction is dictated by the the water concentration gradient. In electrolysis, the membrane is often relatively saturated with water, leading to a small water concentration gradient. Because of this, water transport by diffusion may be small in water electrolysis.[16] However, the gases (hydrogen, oxygen) may diffuse through the membrane due to differences in their partial pressures across the membrane. For hydrogen, this is in particular important for differential pressure electrolysis, where hydrogen is produced at high pressure on the cathode side to reduce the energy requirement in further hydrogen compression before storage; hydrogen is stored at relatively high pressure. Leakage of hydrogen and oxygen through the membrane is problematic because the mixture of oxygen and hydrogen is very reactive/explosive.

Overall, the porous layers (gas-/liquid- diffusion layer) are normally a few $100\,\mu m$ thick, which allows for uniform distribution of reactant/products and electric current. The catalyst on the anode/oxygen side is typically iridium (preferred) or ruthenium with a loading of $1\,mg/cm^2$, while on the cathode/hydrogen side, the catalyst is platinum with a loading of $2\,mg/cm^2$. The catalyst layers are a few micrometers thick; future electrodes may reduce the catalyst loading to half of this.[17] The membrane is typically 100–200 μm thick: a thinner membrane would reduce electric resistance, but increase the problem of gas leakage through the membrane.

2.5. Membrane subsystem

2.5.1. Water sorption vs. temperature

Following Ito et al. (2011), water uptake in Nafion 117 membrane varies with temperature as indicated in Fig. 6.[18]

As seen, for $T \in [20, 90]\,°C$, $\lambda \in [10, 20]$. Figure 6 indicates sorbed water λ fitted to the Hinatsu N-form data (normal form; solid red):

$$\lambda_N = 9.94 + 0.111T + 2.16 \cdot 10^{-4}T^2, \tag{10}$$

---

[16]Small amounts of oxygen and hydrogen may be dissolved in water, and may be carried with dragged and diffused water.

[17]The global production capacity of Iridium is around $9\,tons/year$, which makes the use of Iridium a bottleneck.

[18]Data in Ito et al. (2011) were digitized using WebPlotDigitizer, https://automeris.io/
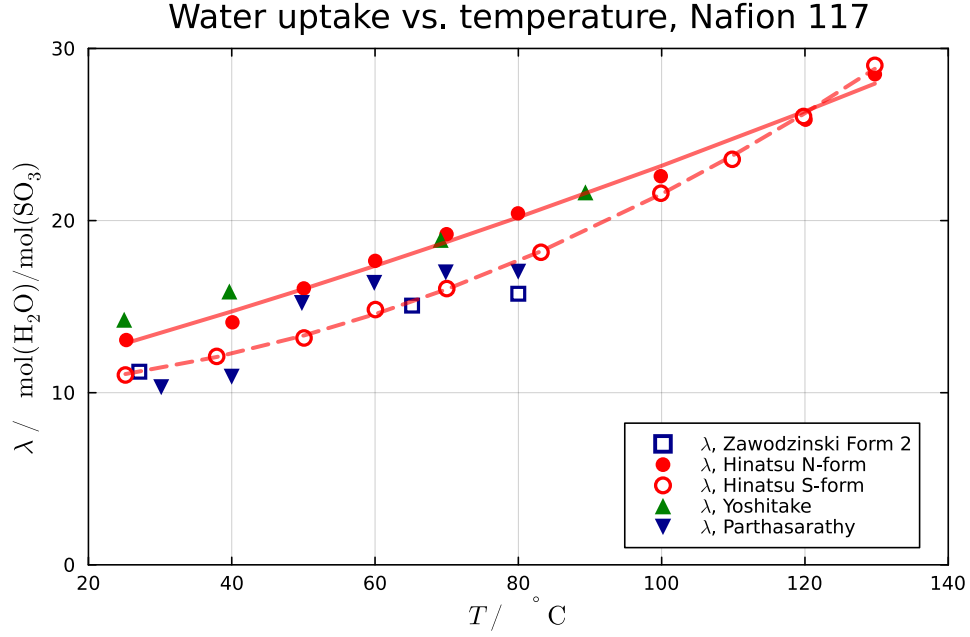
Figure 6: Water uptake/sorption λ in a Nafion 117 membrane immersed in liquid water at different temperatures T.

and to the Hinatsu S-form data (shrunk form), solid dashed:

$$\lambda_{\mathrm{S}} = 10.1 + 1.48 \cdot 10^{-2}T + 9.99 \cdot 10^{-4}T^2. \tag{11}$$

In Eqs. 10 and 11, temperature is given in degrees Celsius.

2.5.2. Fluid transport through the membrane

Fluid is transported through the membrane in 3 ways:

1. By "entrainment" with protons H^+, often referred to as (electro-osmotic) drag (per cell); $\dot{n}_j^{\mathrm{d,c}}$.

2. By diffusion due to variation in chemical potential/concentrations (per cell); $\dot{n}_j^{\delta,\mathrm{c}}$.

3. By force due to pressure differences (per cell), $\dot{n}_j^{\mathrm{p,c}}$.

Drag transport is important, and the transport is proportional to proton flow rate, and thus with electric current. For water saturated membranes in electrolysis, diffusion of water is probably not very important. Diffusion (permeation) of gases, may be important, though. Pressure transport may be important, but we will neglect that here.

2.5.3. Liquid drag through the membrane cell

Liquid transport by drag through a cell is assumed to be proportional to current,

$$\dot{n}_{\mathrm{d,c}} = \eta_{\mathrm{d}} \frac{i'' A_{\mathrm{m}}}{F} \tag{12}$$
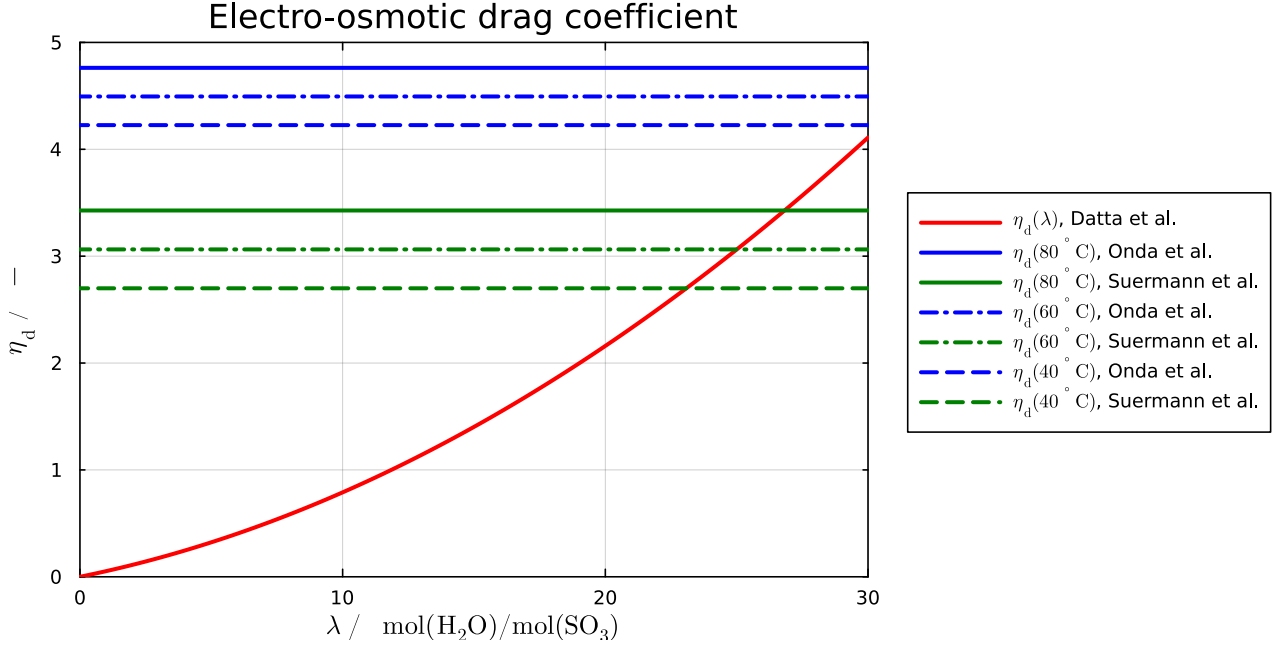
Figure 7: Proposed electro-osmotic drag coefficient for Nafion 117. From Datta et al. (2015), Onda et al. (2002), and Suermann et al. (2017)

where η_d is the (electro-osmotic) drag coefficient. In Dutta et al. (2001), it is proposed that

$$\eta_d = 2.9 \cdot 10^{-3}\lambda^2 + 5 \cdot 10^{-2}\lambda - 3.4 \cdot 10^{-19}$$
$$\Downarrow$$
$$\eta_d \approx 2.9 \cdot 10^{-3}\lambda\left(\lambda + 17.24\right). \tag{13}$$

In Görgün (2006), a difference in λ_a and λ_c was considered, and the average value $\lambda = \frac{\lambda_a + \lambda_c}{2}$ was introduced in the η_d expression of Dutta et al. (2001).

In Onda et al. (2002), a simple temperature dependent relation was proposed as

$$\eta_d = 1.34 \cdot 10^{-2}T + 0.03 \tag{14}$$

with T in Kelvin.

In Suermann et al. (2017), the expression

$$\eta_d = 1.82 \cdot 10^{-2}T - 3.0 \tag{15}$$

is proposed.

Figure 7 depicts the drag coefficient according to Eqs. 13–15.

In other publications, a value of $\eta_d = 0.27$ is proposed; Marangio et al. (2009) changed the value to $\eta_d = 7$ because of an observed large flow rate $\dot{n}_{H_2O}^{d,c}$.

Drag of individual substances j is then given as

$$\dot{n}_j^{d,c} = x_j\dot{n}_{d,c} \tag{16}$$

where x_j is the mole fraction of substance j in the liquid phase.

2.5.4. Membrane proton conductivity

The conductivity κ_{m} of protons is a measure of how easy protons can move through the membrane; κ_{m} depends on the water uptake. Dickinson & Smith (2020) give a class of models for conductivity in a (Nafion) PEM *fuel cell* membrane as

$$\kappa_{\mathrm{m}} = \begin{cases} 0, & \lambda < \lambda_{\min} \\ \kappa_0 \left(\lambda - \lambda_{\min}\right)^{n_\lambda} \exp\left(-\frac{E_{\mathrm{a}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) & \lambda \geq \lambda_{\min}, \end{cases} \tag{17}$$

where κ_0 (S/m) is the conductivity at a reference temperature T_0 (K), $\lambda_{\min}$ (dimensionless) is the minimal water content that gives conductivity, and E_{a}/R (K) is the activation energy per gas constant. Parameters for the Springer model (Springer et al. 1991) of the Nafion 1100 membrane are given by Dickinson & Smith (2020) as

$$\lambda_{\min} = 0.6344$$
$$n_\lambda = 1$$
$$\kappa_0 = 0.5139\,\mathrm{S/m}$$
$$T_0 = 303.15\,\mathrm{K}$$
$$E_{\mathrm{a}}/R = 1268\,\mathrm{K}.$$

Mann et al. (2000) propose an empirical model which also depends on the current density i'' (or: proton flow rate); their model can be re-written in the form

$$\frac{\kappa_{\mathrm{m}}}{\kappa_0} = \begin{cases} 0, & \lambda < \lambda_{\min} + 3\frac{i''}{i''_\varsigma} \\ \dfrac{\left(\lambda - \lambda_{\min} - 3\cdot\frac{i''}{i''_\varsigma}\right)\exp\left(-\frac{E_{\mathrm{a}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)}{1 + 3\cdot 10^{-2}\cdot\frac{i''}{i''_\varsigma} + 6.2\cdot 10^{-2}\cdot\left(\frac{i''}{i''_\varsigma}\right)^{2.5}\left(\frac{T}{T_0}\right)^2}, & \lambda \geq \lambda_{\min} + 3\frac{i''}{i''_\varsigma} \end{cases} \tag{18}$$

with scaling current density $i''_\varsigma = 1\,\mathrm{A/cm^2}$. This model is essentially the same as the one in Eq. 17 for the case $n_\lambda = 1$, with the addition of *current dependency*, and with κ_0 changed to $\kappa_0 = 0.5507\,\mathrm{S/m}$. At zero current density, the models are identical. The model of Mann et al. (2000) has been calibrated with data and a convection model of Eikerling et al. (1998). Figure 8 depicts the current dependence of the product of resistance R_{m} and membrane area A_{m}, $R_{\mathrm{m}} \cdot A_{\mathrm{m}} = \frac{\delta_{\mathrm{m}}}{\kappa_{\mathrm{m}}}$ where δ_{m} is the membrane thickness.

2.5.5. Gas transport through the membrane

Just like for water, the gases hydrogen and oxygen are transported through the membrane in 3 ways:

1. By "entrainment" with protons H$^+$ via water (electro-osmotic) drag; $\dot{n}_j^{\mathrm{d,c}} = x_j^{\mathrm{a}}\dot{n}_{\mathrm{d,c}}$ where it is assumed that gases are dissolved in liquid on the anode side with mole fractions x_j^{a}, $j \in \{\mathrm{H_2}, \mathrm{O_2}\}$, and that water dominates completely in the liquid phase.

2. By diffusion/often denoted permeation due to variation in chemical potential/concentrations; $\dot{n}_j^{\delta,\mathrm{c}}$, $j \in \{\mathrm{H_2}, \mathrm{O_2}\}$.

3. By force due to pressure differences, $\dot{n}_j^{\mathrm{p,c}}$, $j \in \{\mathrm{H_2}, \mathrm{O_2}\}$.

For water, drag transport is important. For gases, the importance of entrainment is uncertain: x_j^{a} will be small.

Transport by pressure difference (total pressure) is probably not very important, and is neglected.

Transport by gas permeation/diffusion will be considered, however.
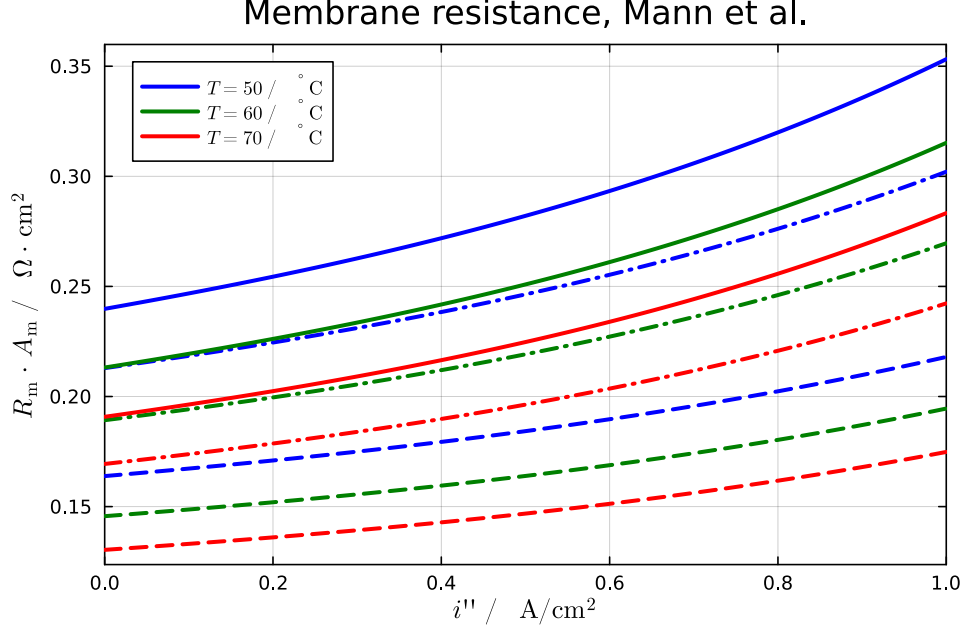
Figure 8: Resistance-area product (unit $\Omega \cdot \mathrm{cm}^2$) for $\delta_\mathrm{m} = 203\,\mu\mathrm{m}$ thick Nafion 117 membrane with water uptake $\lambda = 12.5$ (solid lines), $\lambda = 14$ (dash-dot lines), and $\lambda = 18$ (dashed lines). Case $T = 60\,^\circ\mathrm{C}$ with $\lambda = 12.5$ (blue, solid line) is the case presented in Mann et al. (2000).

2.5.6. Gas diffusion/permeation

Cross flow by concentration induced flux/permeation is often given as

$$\dot{n}_j^{\delta,\mathrm{c}} = \mathcal{J}_j A_\mathrm{m} \tag{19}$$

where $\mathcal{J}_j$ is the molar flux of substance j (amount per time and area); alternatively one could use $\dot{n}_j^{\delta,\prime\prime}$ instead of $\mathcal{J}_j$, but $\mathcal{J}_j$ is so common that it is used here. Molar flux is often given by Fick's law, which in one dimension is

$$\mathcal{J}_j = -\mathcal{D}_j \nabla c_j, \tag{20}$$

with gradient ∇c_j being $\frac{\partial c_j}{\partial x}$ in one-dimensional flow, and $\mathcal{D}_j$ is the diffusion constant. With gas, it is common to use partial pressure p_j instead of concentration, or more generally: fugacity f_j, and write the molar flux as

$$\mathcal{J}_j = -\mathcal{P}_j \nabla f_j \tag{21}$$

where $\mathcal{P}_j$ is the *permeability*; $\nabla f_j \approx \nabla p_j$ for near-ideal gas conditions.

If we assume constant gradient through a membrane from high pressure p_j^+ to low pressure p_j^-, we can thus write

$$\mathcal{J}_j = \mathcal{P}_j \frac{p_j^+ - p_j^-}{\delta_\mathrm{m}} \tag{22}$$

where δ is the thickness of the membrane. In Schalenbach et al. (2013), it is suggested that the pressure at the membrane is higher than that in the separators, as follows:

$$p_j^\mathrm{m} = p + \gamma_j i'' \tag{23}$$

Table 2: Permeability through PEM membrane for hydrogen and oxygen. Taken from Schalenbach (2016), Table C1, ϵ^{dif}.

	Reference value	SI values
$\mathcal{P}_{\mathrm{H_2}}$	$5.31 \cdot 10^{-11}\,\mathrm{mol/s\,cm\,bar}$	$5.31 \cdot 10^{-14}\,\mathrm{mol/s\,m\,Pa}$
$\mathcal{P}_{\mathrm{O_2}}$	$2.26 \cdot 10^{-11}\,\mathrm{mol/s\,cm\,bar}$	$2.26 \cdot 10^{-14}\,\mathrm{mol/s\,m\,Pa}$
$\gamma_{\mathrm{H_2}}$	$8\,\mathrm{bar\,cm^2/A}$	$80\,\mathrm{Pa\,m^2/A}$
$\gamma_{\mathrm{O_2}}$	$9.4\,\mathrm{bar\,cm^2/A}$	$94\,\mathrm{Pa\,m^2/A}$

where p is the separator tank pressure and p_j^{m} is the pressure of $j \in \{\mathrm{H_2, O_2}\}$ at the membrane surface. The expression in Eq. 23 is somewhat unphysical in that with $i'' \equiv 0$, $p_j^{\mathrm{m}} = p$ while the pressure should be $p_j^{\mathrm{m}} = p_j$.

The following values are suggested for permeability by Schalenbach (2016), Table 2; see also Table 5 in Appendix A.

If we neglect the membrane pressure increase according to Eq. 23, Eq. 22 gives hydrogen transport as

$$\mathcal{J}_{\mathrm{H_2}} \approx \mathcal{P}_{\mathrm{H_2}} \frac{p_{\mathrm{H_2}}^{\mathrm{c}} - p_{\mathrm{H_2}}^{\mathrm{a}}}{\delta_{\mathrm{m}}}$$

while for oxygen transport,

$$\mathcal{J}_{\mathrm{O_2}} \approx \mathcal{P}_{\mathrm{O_2}} \frac{p_{\mathrm{O_2}}^{\mathrm{a}} - p_{\mathrm{O_2}}^{\mathrm{c}}}{\delta_{\mathrm{m}}}.$$

In practical operation, the cathode pressure is considerably higher than the anode pressure.

3. Electrolyzer Stack

3.1. System overview

Here, we are mainly interested in the electrolysis of water, with overall reaction

$$\mathrm{H_2O} \rightarrow \mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \tag{24}$$

for the case of $\nu_{\mathrm{e^-}} = 2$, with species vector $\mathrm{S} = (\mathrm{H_2O, H_2, O_2})$, and stoichiometric matrix

$$\nu = \begin{pmatrix} -1 & 1 & \frac{1}{2} \end{pmatrix}. \tag{25}$$

Overall half cell reactions are at the anode (oxidation reaction, OER)

$$\mathrm{H_2O} \rightarrow \frac{1}{2}\mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \tag{26}$$

and at the cathode (reduction reaction, HER)

$$2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{H_2}. \tag{27}$$

It follows that with electron generation rate

$$\dot{n}_{\mathrm{e^-}}^{\mathrm{g}} \triangleq \frac{A_{\mathrm{m}} i''}{F}, \tag{28}$$
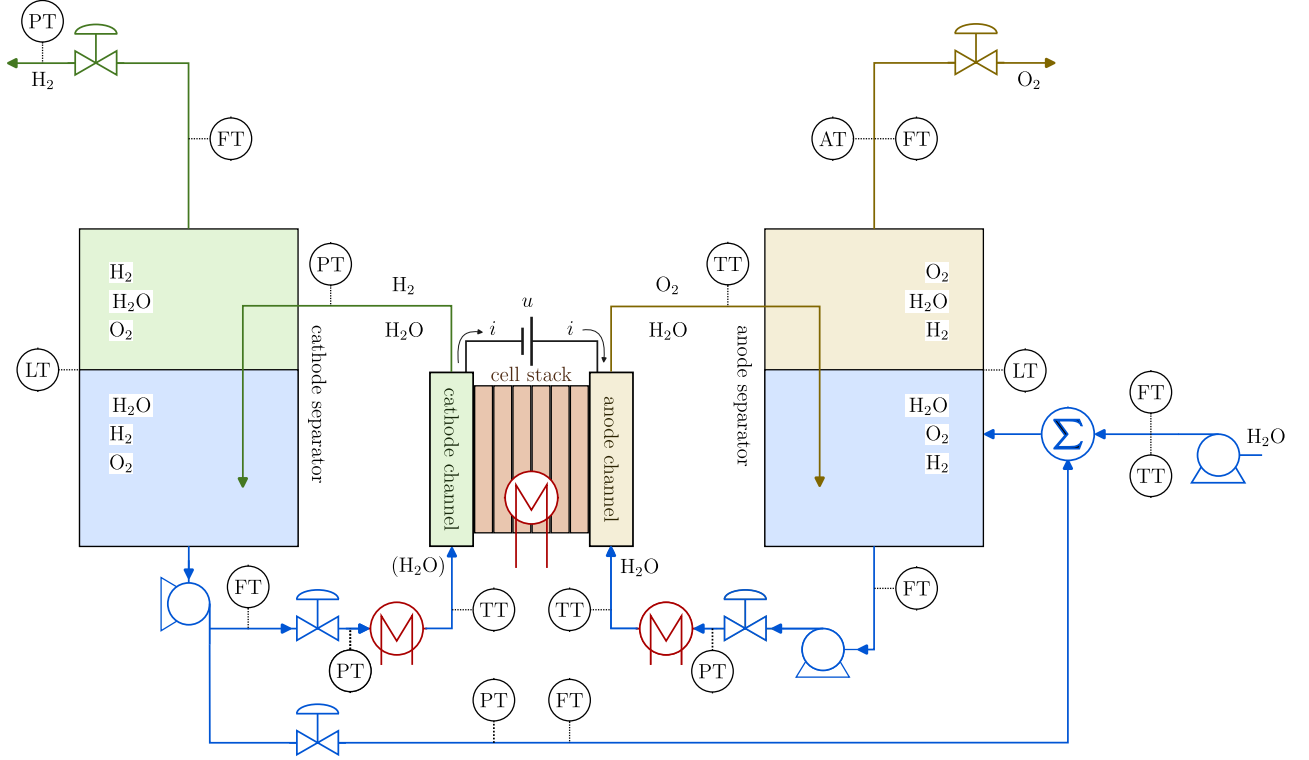
Figure 9: PEM Electrolysis System. Inspired by Onda et al. (2002), Ito et al. (2010), Olivier et al. (2017), Görgün (2006), Crespi et al. (2023).

the rates of the three species in S are

$$\dot{n}_j^{\mathrm{g}} = \frac{\nu_j}{\nu_{\mathrm{e}^-}} \dot{n}_{\mathrm{e}^-}^{\mathrm{g}};\qquad(29)$$

as examples, for each electron reacting, $\nu_1/\nu_{\mathrm{e}^-} = -1/2$ molecules of water are generated (or: consumed, since $\nu_1/\nu_{\mathrm{e}^-} < 0$), while $\nu_3/\nu_{\mathrm{e}^-} = 1/4$ molecules of oxygen are generated.

A PEM electrolyzer system is depicted in Fig. 9.

In Fig. 9, filtered/de-ionized[19] liquid water is fed in from the right to the O_2 separator.[20] Liquid (mainly water) is then pumped out of the bottom of the O_2 separator, flows through a control valve and a heater, before it enters the anode channel. Produced O_2 gas in the electrolyzer *cell stack* between the anode and cathode channels, and liquid water feed minus consumption/leakage, are lead out of the anode channel and into the O_2 separator. Gas flashed off in the anode liquid/gas separator, leaves through the top of the separator.

Produced H_2 gas in the electrolyzer cell stack as well as liquid transported through the membranes of the cell stack are lead out of the cathode channel and into the H_2 separator. Gas flashed off in the cathode liquid/gas separator, leaves through the top, and flows to some storage facility. Liquid (mainly water, but some dissolved H_2 and possibly O_2) in cathode liquid/gas separator is re-circulated/pumped back to the water feed of the anode separator, or may in principle also be circulated through the cathode

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[19]De-ionization is necessary to reduce ions in water. Ions in water lead to stray currents through the membrane.

[20]In most references, the O_2 separator/anode part is depicted on the left side and the H_2 separator/-cathode part on the right side; here this is mirrored. The reason for mirroring the cathode side and the anode side here, is to make the locations consistent with the PEM electrolysis cell in Fig. 5.

channel. Such a circulation of water through the cathode channel is not necessary, unless it is used to stabilize the temperature in the electrolyzer stack; the corresponding valve is thus often closed.

In Fig. 9, a number of sensor transmitters are indicated[21]. The analysis transmitter (AT) at the gas outlet from the anode separator may be included for safety reasons: it may be of interest to measure and ensure that the hydrogen content in oxygen is below the flammability/explosion level.[22] Typically, flow sensors (FT) may help to control flow rates, level sensors (LT) may be needed in controllers to keep constant liquid levels in the separators, pressure sensors are needed to keep pressures at desired levels, while temperature sensors (TT) are needed to keep the system at the desired temperature. Figure 9 indicates three heaters/coolers which may be used to manipulate the system temperature.

Observe that industrial systems are more complex. See, e.g., Pettersen et al. (2024) for more details.

The electrolyzer stack consists of multiple electrolyzer cells stacked together by connecting bipolar plates, with flow from separators fed in parallel through the cell channels.

3.2. Overview of generation/transport

Table 3 gives a summary of generation/transport terms in the electrolyzer stack.

Details about generation/flow terms are given in the subsequent sections.

3.3. VT flash

3.3.1. What is VT flash?

Suppose we have a tank at time t of volume V and temperature T, with amount n_{H_2O} of water and amount n_j of additional light gases (e.g., hydrogen, oxygen). We consider the possibility that the substances in volume V in a *flash* splits into liquid phase and gas phase.

In VT flash, we know volume V (geometric property), temperature T (from energy balance?), and "pre-flash" amounts $\mathbf{n} = (n_{H_2O}, n_2, \ldots, n_{N_s})$ (from species balance) for all N_s substances. Then we ask the question: "post-flash", i.e., after the splitting into liquid and gas phases takes place, what are equilibrium values of :

1. Mole fractions of the substances in the liquid phase, $x = (x_{H_2O}, x_2, \ldots)$; these are by definition $x_j = \frac{n_j^\ell}{n_\ell}$,

2. Mole fractions of the substances in the gas phase, $x = (y_{H_2O}, y_2, \ldots)$; by definition $y_j = \frac{n_j^g}{n_g}$,

3. Amounts in the liquid phase, n_ℓ, and in the gas phase, n_g,

4. Pressure p in the tank,

---

[21]Sensors are indicated by circles holding two letters. The first letter A, F, L, P, T, refers to analysis, flow, level, pressure, and temperature, respectively. The second letter T indicates *transmitter*.

[22]Hydrogen permeates through the membrane to the anode side, and oxygen permeates to the cathode side and cause a similar problem. Dissolved light gases (hydrogen, oxygen) may also be dragged by water through the membrane. Light gases are dissolved in the liquid (mainly water), and is re-circulated back form the cathode separator to the anode separator.

Table 3: Generation/transport terms in PEM electrolysis. "#" is section no., "**C**" is cathode, "**F**" is flow, "**A**" is anode, "**I**" indicates importance. **F**: $\rightarrow$, $\leftarrow$ flow through the membrane; $\uparrow$, $\downarrow$ do not cross the membrane. **I**: + implies important terms, ? implies terms to consider. Terms in **#1** involve the membrane. Terms in **#2** include both anode and cathode volumes. Terms in **#3** involve the cathode volume. Terms in **#4** involve the anode volume.

#	**C**	**F**	**A**	Symbol	**I**	Description
1	—	$\downarrow$	H_2O	$\dot{n}_{H_2O}^{g}$	+	Consumption by combination with O_2
1	—	$\uparrow$	O_2	$\dot{n}_{O_2}^{g}$	+	Generation by combination with H_2O
1	H_2	$\uparrow$	—	$\dot{n}_{H_2}^{g}$	+	Generation by combination of electron with proton
1	H_2O	$\leftarrow$	H_2O	$\dot{n}_{H_2O}^{d}$	+	Drag of water via protons through membrane, proportional to i''
1	O_2	$\leftarrow$	O_2	$\dot{n}_{O_2}^{d}$	?	Drag of dissolved oxygen with water through membrane, proportional to i''
1	H_2	$\leftarrow$	H_2	$\dot{n}_{H_2}^{d}$	?	Drag of dissolved hydrogen with water through membrane, proportional to i''
1	H_2	$\rightarrow$	H_2	$\dot{n}_{H_2}^{\delta}$	?	Diffusion/permeation of hydrogen through membrane due to partial pressure difference
1	O_2	$\leftarrow$	O_2	$\dot{n}_{O_2}^{\delta}$	?	Diffusion/permeation of oxygen through membrane due to partial pressure difference
2	H_2O	$\rightarrow$	H_2O	$\dot{n}_{H_2O}^{c,r}$	+	Recirculation of water from cathode to anode
2	O_2	$\rightarrow$	O_2	$\dot{n}_{O_2}^{c,r}$	?	Resirculation of oxygen via water from cathode to anode
2	H_2	$\rightarrow$	H_2	$\dot{n}_{H_2}^{c,r}$	?	Resirculation of hydrogen via water from cathode to anode
3	H_2O	$\downarrow$	—	$\dot{n}_{H_2O}^{c,e}$	?	Release to hydrogen storage subsystem via cathode effluent valve
3	H_2	$\downarrow$	—	$\dot{n}_{H_2}^{c,e}$	+	Release to hydrogen storage subsystem via cathode effluent valve
3	O_2	$\downarrow$	—	$\dot{n}_{O_2}^{c,e}$	?	Release to hydrogen storage subsystem via cathode effluent valve
4	—	$\uparrow$	H_2O	$\dot{n}_{H_2O}^{i}$	+	Injection of fresh water from water supply system
4	—	$\downarrow$	H_2O	$\dot{n}_{H_2O}^{a,e}$	?	Release of water to atmosphere via anode effluent valve
4	—	$\downarrow$	O_2	$\dot{n}_{O_2}^{a,e}$	+	Release of oxygen to atmosphere via anode effluent valve
4	—	$\downarrow$	H_2	$\dot{n}_{H_2}^{a,e}$	?	Release of hydrogen to atmosphere via anode effluent valve

5. Liquid volume V_ℓ, and gas volume $V_{\mathrm{g}} = V - V_\ell$.

In this project, we will assume that the separator tanks flash instantaneously and immediately reach equilibrium. In general, equilibrium computations are complex.

3.3.2. Equilibrium conditions

At equilibrium, both liquid and gas phases are assumed to be homogeneous, with the same temperature T in both phases, and the same pressure p in both phases. Furthermore, at equilibrium, the so-called "chemical potential" μ of a particular substance must be the same in the liquid phase and the gas phase, $\mu_j^\ell = \mu_j^{\mathrm{g}}$. In some presentations, chemical potential is transformed to "fugacity" f, and equilibrium requires $f_j^\ell = f_j^{\mathrm{g}}$.

3.3.3. Simplifying assumptions

We will make the following simplifying assumptions:

1. The dominant liquid substance *water* follows Raoult's law for the liquid phase,

$$f_{\mathrm{H_2O}}^\ell (T, p, x) \approx x_{\mathrm{H_2O}} f_{\mathrm{H_2O}}^{\ell,\star} (T, p)$$

where $f_{\mathrm{H_2O}}^{\ell,\star} (T, p)$ is the hypothetical pure water fugacity. We will make two additional sub-assumptions,

   a) Water is so dominant that at first, we set $x_{\mathrm{H_2O}} = 1$,

   b) Pure water fugacity is independent of pressure and equal to the water saturation fugacity, and

$$f_{\mathrm{H_2O}}^\ell (T, p, x) \approx f_{\mathrm{H_2O}}^{\ell,\star} (T, p) \approx f_{\mathrm{H_2O}}^{\ell,\mathrm{sat}} (T). \tag{30}$$

   c) Because water is so dominant in the liquid phase, the molar volume of the liquid phase $\tilde{V}_\ell (T, p, x)$ is approximately equal to the pure water molar volume $\tilde{V}_{\mathrm{H_2O}}^{\ell,\star} (T, p)$. We further assume this is close to the saturation water molar volume, $\tilde{V}_{\mathrm{H_2O}}^{\ell,\mathrm{sat}} (T)$:

$$\tilde{V}_\ell (T, p, x) \approx \tilde{V}_{\mathrm{H_2O}}^{\ell,\mathrm{sat}} (T). \tag{31}$$

2. The light gases have very low fraction in the liquid phase, and follows Henry's law,

$$f_j^\ell (T, p, x) \approx x_j \cdot \mathcal{H}_{j,\mathrm{H_2O}} (T, p) \approx x_j \cdot \mathcal{H}_{j,\mathrm{H_2O}} (T, p) \tag{32}$$

valid for $j \in \{\mathrm{H_2}, \mathrm{O_2}, \mathrm{N_2}, \ldots\}$. We will neglect the pressure dependence, and set $\mathcal{H}_{j,\mathrm{H_2O}} (T, p) \approx \mathcal{H}_{j,\mathrm{H_2O}} (T)$. Here, Henry's constant/correlation $\mathcal{H}_{j,\mathrm{H_2O}}$ has a form that varies with both the light gas substance j and the dominant substance ($\mathrm{H_2O}$ in $\mathcal{H}_{j,\mathrm{H_2O}}$). In other words, if we also consider dissolution of light gases in, say gasoline, $\mathcal{H}_{j,\mathrm{H_2O}} (T) \neq \mathcal{H}_{j,\mathrm{gasoline}} (T)$.

3. In the gas phase, all substances behave as ideal gas, and

$$f_j^{\mathrm{g}} (T, p, y) \approx p_j = y_j \cdot p. \tag{33}$$

3.3.4. Notation

In general, we will write a vector of elements n_j (amount) as

$$\mathbf{n} = (n_1, \ldots, n_{N_\mathrm{s}})$$

and let n denote the sum of elements in $\mathbf{n}$, i.e., $n = \sum_{j=1}^{N_\mathrm{s}} n_j$. If we consider elements in the liquid or gas phase, we add subscript ℓ or g, e.g., $\mathbf{n}_\ell$ and n_ℓ. However, if the sum of elements in a vector is not important, we will avoid bold face in the vector, thus

$$x = (x_1, \ldots, x_{N_\mathrm{s}})$$

where x is the vector of mole fractions; the sum is not important since we know that $\sum_{j=1}^{N_\mathrm{s}} x_j \equiv 1$, and we do not need a special symbol for that.

3.3.5. VT flash algorithm

Based on Raoult's law for liquid water, Henry's law for dissolved light gases, and ideal gas law for the gas phase, a VT flash algorithm will have the following form.

Known: System volume V, temperature T, and amount vector $\mathbf{n} = (n_{\mathrm{H_2O}}, n_2, \ldots, n_{N_\mathrm{s}})$ are known. Furthermore, we know functions $f_{\mathrm{H_2O}}^{\ell,\mathrm{sat}}(T)$ and $\mathcal{H}_{j,\mathrm{H_2O}}(T)$ for $j \in \{2, \ldots, N_\mathrm{s}\}$, as well as water molar volume $\tilde{V}_{\mathrm{H_2O}}^{\ell,\mathrm{sat}}(T)$.

Step 1: Approximate partial water pressure,

$$p_{\mathrm{H_2O}} \approx p_{\mathrm{H_2O}}^{\ell,\mathrm{sat}}(T). \tag{34}$$

Step 2: With

$$n_{\mathrm{H_2O}} = \mathbf{n}_1, \tag{35}$$

assume first that

$$n_j^\mathrm{g} \approx n_j, \quad j \geq 2 \tag{36}$$

Step 3: Water in liquid and gas phase:

$$n_{\mathrm{H_2O}}^\ell = \frac{f_{\mathrm{H_2O}}^{\ell,\mathrm{sat}} \cdot V - n_{\mathrm{H_2O}} RT}{f_{\mathrm{H_2O}}^{\ell,\mathrm{sat}} \cdot \tilde{V}_{\mathrm{H_2O}}^\ell - RT} \tag{37}$$

$$n_{\mathrm{H_2O}}^\mathrm{g} = n_{\mathrm{H_2O}} - n_{\mathrm{H_2O}}^\ell. \tag{38}$$

Water is thus conserved.

Step 4: Phase volumes,

$$V_\ell \approx n_{\mathrm{H_2O}}^\ell \cdot \tilde{V}_{\mathrm{H_2O}}^{\ell,\mathrm{sat}}(T) \tag{39}$$

$$V_\mathrm{g} = V - V_\ell. \tag{40}$$

Step 5: Partial pressure and total pressure,

$$p_j \approx \frac{n_j^\mathrm{g} RT}{V_\mathrm{g}} \tag{41}$$

$$p = p_{\mathrm{H_2O}} + \sum_{j=2}^{N_\mathrm{s}} p_j. \tag{42}$$

Step 6: Temporary phase amounts (light gases are not conserved)

$$\mathbf{n}_\mathrm{g} = \left(n_{\mathrm{H_2O}}^\mathrm{g}, \mathbf{n}_{2:N_\mathrm{s}}\right) \tag{43}$$

$$y = \frac{\mathbf{n}_\mathrm{g}}{n_\mathrm{g}} = \frac{\mathbf{n}_\mathrm{g}}{\sum_{j=1}^{N_\mathrm{s}} \mathbf{n}_{\mathrm{g},j}} \tag{44}$$

$$\mathbf{n}_\ell = n_{\mathrm{H_2O}}^\ell \cdot \left(1, j \in \{2,\dots,N_\mathrm{s}\} : \frac{p y_j}{\mathcal{H}_{j,\mathrm{H_2O}}}\right) \tag{45}$$

$$x = \frac{\mathbf{n}_\ell}{n_\ell} = \frac{\mathbf{n}_\ell}{\sum_{j=1}^{N_\mathrm{s}} \mathbf{n}_{\ell,j}}. \tag{46}$$

Step 7: *Correction* to ensure mole conservation of light gases. Assuming that V_ℓ, V_g, $\mathbf{n}_\ell$, and x are correct at the end of Step 6,

$$\mathbf{n}_\mathrm{g} = \mathbf{n} - \mathbf{n}_\ell \tag{47}$$

$$y = \frac{\mathbf{n}_\mathrm{g}}{n_\mathrm{g}} \tag{48}$$

$$p = p_{\mathrm{H_2O}} + \sum_{j=2}^{N_\mathrm{s}} \frac{n_{\mathrm{g},j} R T}{V_\mathrm{g}} \tag{49}$$

$$\tilde{V}_\mathrm{g} = \frac{V_\mathrm{g}}{n_\mathrm{g}} \tag{50}$$

$$\tilde{V}_\ell = \frac{V_\ell}{n_\ell}. \tag{51}$$

Return: Computed values x (Eq. 46), y (Eq. 48), n_ℓ (Eq. 45), n_g (Eq. 47), $\tilde{V}_\ell$ (Eq. 51), $\tilde{V}_\mathrm{g}$ (Eq. 50), p (Eq. 49).

3.3.6. Temperature functions

Approximate water saturation functions with absolute temperature T in Kelvin:

$$f_{\mathrm{H_2O}}^{\ell,\mathrm{sat}}(T) = \varphi_{\mathrm{H_2O}}^{\ell,\mathrm{sat}}(T) \cdot p_{\mathrm{H_2O}}^{\mathrm{sat}}(T) \tag{52}$$

with

$$\varphi_{\mathrm{H_2O}}^{\ell,\mathrm{sat}}(T) = 1.0012 - 1.6 \cdot 10^{-3} \exp\left(8.7 \frac{T - 273.15}{373.15}\right) \tag{53}$$

$$\log_{10} \frac{p_{\mathrm{H_2O}}^{\mathrm{sat}}(T)}{p^\varsigma} = A_{\mathrm{H_2O}} - \frac{B_{\mathrm{H_2O}}}{C_{\mathrm{H_2O}} + T - 273.15} \tag{54}$$

where Antoine correlation parameters are provided in Table 5 of Appendix A for $p^\varsigma = 1\,\mathrm{bar}$.

Liquid molar volume for water is given in a limited temperature range as

$$\tilde{V}_{\mathrm{H_2O}}^{\ell,\mathrm{sat}}(T) = \frac{2.23 - 3.332 \cdot 10^{-3} T + 6.421 \cdot 10^{-6} T^2}{10^5}. \tag{55}$$

Light gas Henry correlations:

$$\mathcal{H} = \mathcal{H}_{\max} \bar{\mathcal{H}}, \tag{56}$$

Table 4: Henry's constant data. From Himmelblau (1960).

Gas:	O_2	N_2	H_2	He	Xe	CH_4
$\mathcal{H}_{max} \cdot 10^{-4}$, $\mathcal{H}_{max}$ in atm	7.08	12.39	7.54	14.99	3.17	7.02
$\frac{1}{T_{max}} \cdot 10^3$, T_{max} in K	2.73	2.80	3.09	3.26	2.61	2.71

where $\mathcal{H}$ has the unit of *pressure*. Introduce *dimensionless* $\bar{T}$

$$\frac{1}{\bar{T}} \triangleq \frac{\frac{1}{T} - \frac{1}{T_c^{H_2O}}}{\frac{1}{T_{max}} - \frac{1}{T_c^{H_2O}}}. \tag{57}$$

Here, $\mathcal{H}_{max}$, T_{max} depend on the dissolved substance (light gas), $T_c^{H_2O}$ is the critical temperature of the solvent (here: water), and *dimensionless* $\bar{\mathcal{H}}$ is found from the correlation

$$-\log_{10}\bar{\mathcal{H}} = 1.142 - 2.846\frac{1}{\bar{T}} + 2.486\frac{1}{\bar{T}^2} - 0.9761\frac{1}{\bar{T}^3} + 0.2001\frac{1}{\bar{T}^4}. \tag{58}$$

The following data are given, Table 4; see also Table 5 of Appendix A including relevant critical temperatures.

3.4. Fluid transport equipment

3.4.1. Valve flow rate

The valve model of Instrument Society of America (ISA), the ANSI/ISA S75.01 standard[23], can be written in dimensionless form as

$$\frac{\dot{m}_v}{\dot{m}_v^c} = f\left(u_v\right) \cdot \eta_p \cdot Y \cdot \sqrt{\frac{\Delta p}{p^\varsigma} \cdot \frac{\rho_i}{\rho^\varsigma}} \tag{59}$$

where:

- $\dot{m}_v$: valve mass flow rate,

- $\dot{m}_v^c$: valve mass flow rate capacity,

- $u_v \in [0,1]$: valve control signal (specifies valve opening) with valve characteristic $f : [0,1] \rightarrow [0,1]$,

- η_p: dimensionless piping efficiency factor,

- Y: expansion factor,

- ρ_i: influent density,

- $\Delta p \triangleq p_i - p_e$: pressure drop across valve; p_i, p_e are influent and effluent pressures, respectively,

- $\rho^\varsigma, p^\varsigma$: scaling density and pressure, respectively.

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[23]http://integrated.cc/cse/ISA_750101_SPBd.pdf , accessed December 13, 2023

Piping efficiency factor η_{p} describes fractional mass flow loss due to flanges in the piping system that were not present in the laboratory set-up used to find valve parameters. For constant density fluids, expansion factor $Y \equiv 1$, while for compressible fluids, Y is given by

$$Y = 1 - \min\left(1, \frac{\Delta p/p_{\mathrm{i}}}{3\gamma_{\mathrm{r}}x_{\mathrm{c}}}\right) \qquad (60)$$

where x_{c} is the *choking relative pressure drop* and is a valve parameter provided by the valve manufacturer, while γ_{r} is the specific heat ratio of the fluid relative to the diatomic ideal gas specific heat ratio,

$$\gamma_{\mathrm{r}} = \frac{\hat{c}_{\mathrm{p}}/\hat{c}_{\mathrm{v}}}{(\hat{c}_{\mathrm{p}}/\hat{c}_{\mathrm{v}})_{\mathrm{diatomic}}^{\mathrm{ideal\,gas}}} \qquad (61)$$

with $\hat{c}_{\mathrm{p}}, \hat{c}_{\mathrm{v}}$ being the specific heat capacities at constant pressure and volume, respectively. For diatomic ideal gases, $\tilde{c}_{\mathrm{v}} = \frac{5}{2}R$ and $\tilde{c}_{\mathrm{p}} = \tilde{c}_{\mathrm{v}} + R$, thus

$$\left.\frac{\hat{c}_{\mathrm{p}}}{\hat{c}_{\mathrm{v}}}\right|_{\mathrm{diatomic}}^{\mathrm{ideal\,gas}} = \left.\frac{\tilde{c}_{\mathrm{p}}}{\tilde{c}_{\mathrm{v}}}\right|_{\mathrm{diatomic}}^{\mathrm{ideal\,gas}} = \frac{\frac{5}{2}R + R}{\frac{5}{2}R} = \frac{7}{5} = 1.4. \qquad (62)$$

3.4.2. Simplified valve model

Neglecting piping efficiency losses, we have

$$\eta_{\mathrm{p}} = 1.$$

For simplicity, assume that x_{c} satisfies

$$\gamma_{\mathrm{r}}x_{\mathrm{c}} = \frac{1}{2}.$$

This gives

$$\frac{\dot{m}_{\mathrm{v}}}{\dot{m}_{\mathrm{v}}^{\mathrm{c}}} = f\left(u_{\mathrm{v}}\right) \cdot Y \cdot \sqrt{\frac{\Delta p}{p^{\mathrm{s}}} \cdot \frac{\rho_{\mathrm{i}}}{\rho^{\mathrm{s}}}}$$

with

$$Y = 1 - \min\left(1, \frac{2}{3}\frac{\Delta p}{p_{\mathrm{i}}}\right).$$

In order to avoid problems with flow reversal, consider replacing Δp with $\max\left(0, \Delta p\right)$.

3.4.3. Pump flow rate

Pumps are normally used to transport liquids, but in practice the liquid may contain gas. Here, we will assume that a pure liquid is considered.

For flow of fluid with density ρ and viscosity μ in a pipe with diameter D and length L, it can be shown from dimensional analysis that velocity v and pressure drop Δp are related as

$$F\left(\frac{\Delta p}{\rho v^2}, \frac{\rho v D}{\mu}, \frac{L}{D}\right) = 0.$$

For a pump, we will neglect L/D. The second group in the function is recognized as the Reynolds number N_{Re}. If we introduce volumetric flow rate $\dot{V}_{\mathrm{p}} = Av$, we would expect

the form

$$F_1 \left(\frac{\Delta p \cdot A^2}{\rho \dot{V}_{\mathrm{p}}^2}, N_{\mathrm{Re}} \right) = 0$$

$$\Downarrow$$

$$\frac{\Delta p \cdot A^2}{\rho \dot{V}_{\mathrm{p}}^2} = G^2 \left(N_{\mathrm{Re}} \right)$$

or

$$\dot{V}_{\mathrm{p}} = \frac{A}{G \left(N_{\mathrm{Re}} \right)} \sqrt{\frac{\Delta p}{\rho}}.$$

It follows that

$$\dot{m}_{\mathrm{p}} = \rho \dot{V}_{\mathrm{p}} = \frac{A}{G \left(N_{\mathrm{Re}} \right)} \sqrt{\Delta p \cdot \rho}.$$

By introducing scaling parameters, we find

$$\dot{m}_{\mathrm{p}} = \frac{\sqrt{p^{\varsigma} \rho^{\varsigma} A^2}}{G \left(N_{\mathrm{Re}} \right)} \sqrt{\frac{\Delta p}{p^{\varsigma}} \cdot \frac{\rho}{\rho^{\varsigma}}}.$$

Here, we observe that $p^{\varsigma} \rho^{\varsigma} A^2$ has SI unit $\frac{\mathrm{N}}{\mathrm{m}^2} \cdot \frac{\mathrm{kg}}{\mathrm{m}^3} \cdot \mathrm{m}^4 = \frac{\mathrm{kg \cdot m/s^2}}{\mathrm{m}^2} \cdot \frac{\mathrm{kg}}{\mathrm{m}^3} \cdot \mathrm{m}^4 = \frac{\mathrm{kg}^2}{\mathrm{s}^2}$, which is the unit of mass flow rate squared, while $G \left(N_{\mathrm{Re}} \right)$ is dimensionless. We can thus interpret

$$\frac{\sqrt{p^{\varsigma} \rho^{\varsigma} A^2}}{G \left(N_{\mathrm{Re}} \right)} \triangleq \dot{m}_{\mathrm{p}}^{\mathrm{c}} \cdot \eta \left(N_{\mathrm{Re}} \right)$$

where $\dot{m}_{\mathrm{p}}^{\mathrm{c}}$ is the pump capacity, while $\eta \left(N_{\mathrm{Re}} \right)$ is some pump efficiency that varies with the Reynolds number. In practice, it is possible to change the flow rate by manipulating a pump signal u_{p} which influences the motor speed of the pump. Thus, we can write the pump model in the dimensionless form

$$\frac{\dot{m}_{\mathrm{p}}}{\dot{m}_{\mathrm{p}}^{\mathrm{c}}} = f \left(u_{\mathrm{p}} \right) \cdot \eta_{\mathrm{p}} \left(N_{\mathrm{Re}} \right) \cdot \sqrt{\frac{\Delta p}{p^{\varsigma}} \cdot \frac{\rho}{\rho^{\varsigma}}} \qquad (63)$$

where $u_{\mathrm{p}} \in [0, 1]$ and $f : [0, 1] \to [0, 1]$. Observe the similarity to the valve model; the essential difference is that (i) because the density of liquids is more or less constant, we do not need the expansion factor Y, and (ii) there is an efficiency factor η_{p} which combines piping efficiency (fittings, etc.) and internal efficiency in the pump related to viscosity, etc., of the fluid (N_{Re}).

3.4.4. Simplified pump model

We will neglect piping efficiency losses and internal viscosity losses, thus we set

$$\eta_{\mathrm{p}} = 1.$$

In addition, we will neglect the dependence on pressure drop and density. Thus we assume that

$$\frac{\dot{m}_{\mathrm{p}}}{\dot{m}_{\mathrm{p}}^{\mathrm{c}}} = f \left(u_{\mathrm{p}} \right).$$

Here, we can alternatively use $\dot{m}_{\mathrm{p}}$ directly as control variable (instead of u_{p}), with the constraint that $\dot{m}_{\mathrm{p}} \in \left[0, \dot{m}_{\mathrm{p}}^{\mathrm{c}} \right]$.

3.4.5. Flow rates in mixtures

With a mixture of N_s substances in a separator tank of volume V, we seek the flow rate of each substance. We will consider flow from homogeneous parts of a separator tank; either the gas or liquid volume.

From a dynamic model, assume that states $\mathbf{n}$ and T known, together with the separator tank volume V. By doing VT flash (Section 3.3), we essentially find:

$$(T, \mathbf{n}; V) \overset{\text{VT flash}}{\longrightarrow} \left(x, y, n_\ell, n_g, \tilde{V}_\ell, \tilde{V}_g, p \right). \tag{64}$$

The mass flow rate $\dot{m}_j$ of substance j from the considered homogeneous volume equals the total mass flow rate $\dot{m}$, multiplied by the mass fraction ω_j of substance j,

$$\dot{m}_j = \omega_j \dot{m}. \tag{65}$$

Mass flow rate ω_j can be expressed by mole fractions. In the following expressions, Eqs. 66–70, we use the homogeneous symbols for liquid: $\mathbf{n}_\ell$, n_ℓ, x, and V_ℓ; if the homogeneous mixture is gas, these are replaced y $\mathbf{n}_g$, n_g, y, and V_g:

$$\omega_j = \frac{m_j}{\sum_{j=1}^{N_s} m_j} = \frac{n_j M_j}{\sum_{j=1}^{N_s} n_j M_j} = \frac{x_j M_j n_\ell}{\sum_{j=1}^{N_s} x_j M_j n_\ell} = \frac{x_j M_j}{\sum_{j=1}^{N_s} x_j M_j}. \tag{66}$$

Molar flow rate $\dot{n}_j = \dot{m}_j / M_j$ is then

$$\dot{n}_j = \frac{\dot{m}_j}{M_j} = \frac{\omega_j \dot{m}}{M_j} = \frac{x_j}{\sum_{j=1}^{N_s} x_j M_j} \cdot \dot{m}. \tag{67}$$

Here, we can introduce

$$\dot{n} = \frac{\dot{m}}{\sum_{j=1}^{N_s} x_j M_j} \tag{68}$$

and

$$\dot{n}_j = x_j \cdot \dot{n}. \tag{69}$$

Density ρ_i of the mixture in the homogeneous volume V is

$$\rho_i = \frac{m_\ell}{V_\ell} = \frac{\sum_{j=1}^{N_s} n_j^\ell M_j}{V_\ell} = \frac{n_\ell \sum_{j=1}^{N_s} x_j M_j}{V_\ell} = \frac{\sum_{j=1}^{N_s} x_j M_j}{\tilde{V}}. \tag{70}$$

Again, if the mixture is in the gas phase instead, symbols $\mathbf{n}_\ell$, n_ℓ, x, and V_ℓ are simply replaced by $\mathbf{n}_g$, n_g, y, and V_g, respectively.

3.5. Anode volume

With reference to Fig. 9, the anode separator system can be depicted as in Fig. 10.

The anode separator volume will contain water (H_2O, mainly in liquid form) and oxygen (O_2, mainly in gas form), with some fraction of hydrogen (H_2, mainly in gas form).

With N_c electrolysis cells in the electrolysis stack,

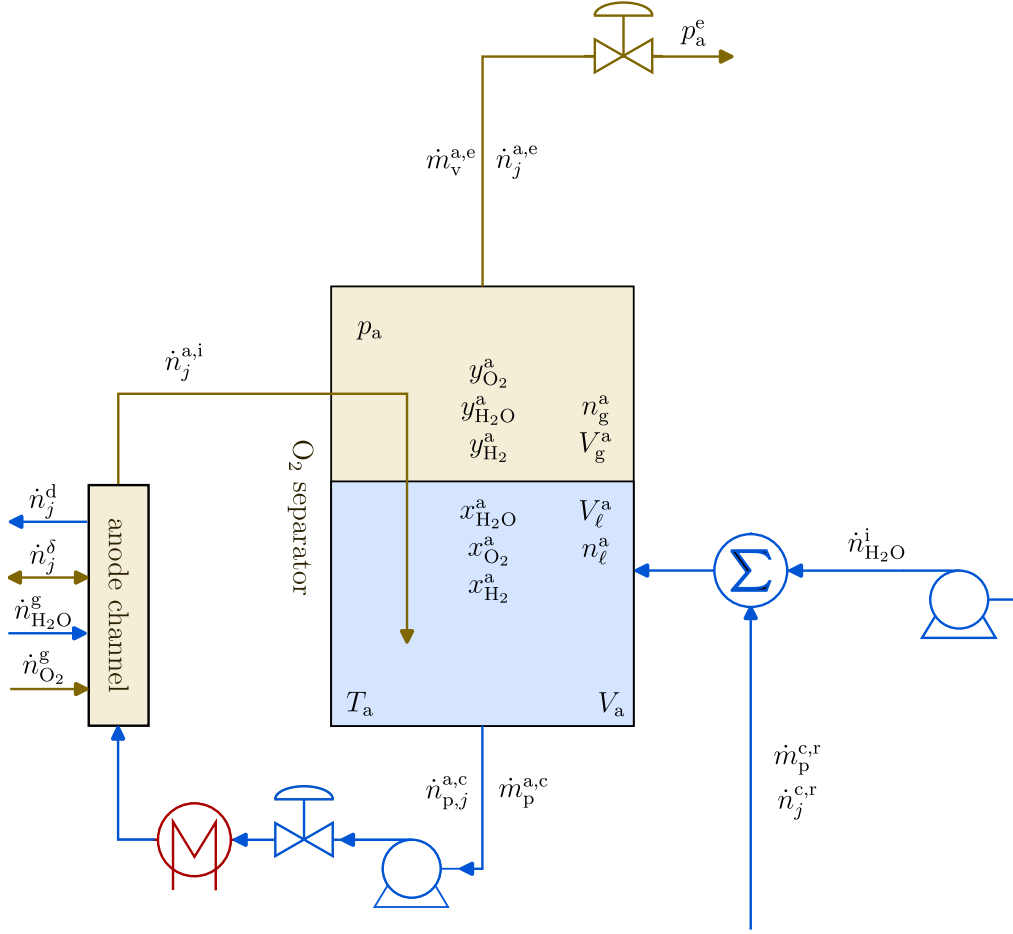$$\dot{n}_{H_2O}^g = N_c \cdot \frac{\nu_{H_2O}}{\nu_{e^-}} \frac{A_m i''}{F} \tag{71}$$

Figure 10: Anode separator subsystem. Note that generation $\dot{n}_{H_2O}^g$ is negative (consumption), which means that the actual flow is against the arrow direction.

while
$$\dot{n}_{\mathrm{O_2}}^{\mathrm{g}} = N_{\mathrm{c}} \cdot \frac{\nu_{\mathrm{O_2}}}{\nu_{\mathrm{e^-}}} \frac{A_{\mathrm{m}} i''}{F}. \tag{72}$$

With known anode separator amount vector $\mathbf{n}_{\mathrm{a}} = \left(n_{\mathrm{H_2O}}^{\mathrm{a}}, n_{\mathrm{H_2}}^{\mathrm{a}}, n_{\mathrm{O_2}}^{\mathrm{a}} \right)$, anode volume V_{a}, and anode temperature T_{a}, VT flash as in Section 3.3 provides anode mole fractions $x_{\mathrm{a}} = \left(x_{\mathrm{H_2O}}^{\mathrm{a}}, x_{\mathrm{H_2}}^{\mathrm{a}}, x_{\mathrm{O_2}}^{\mathrm{a}} \right)$, $y_{\mathrm{a}} = \left(y_{\mathrm{H_2O}}^{\mathrm{a}}, y_{\mathrm{H_2}}^{\mathrm{a}}, y_{\mathrm{O_2}}^{\mathrm{a}} \right)$, as well as anode liquid and gas volumes V_{ℓ}^{a} and $V_{\mathrm{g}}^{\mathrm{a}}$, and anode pressure p_{a}.

Liquid will be dragged through the membrane via the proton (H$^+$) transport. For each cell,
$$\dot{n}_{\mathrm{d,c}} = \eta_{\mathrm{d}} \cdot \frac{A_{\mathrm{m}} i''}{F}; \tag{73}$$

assume the expression for electro-osmotic drag coefficient taken from Eq. 14,

$$\eta_{\mathrm{d}} = 1.34 \cdot 10^{-2} T + 0.03 \tag{74}$$

where T is given in K. The total drag through the stack is thus

$$\dot{n}_{\mathrm{d}} = N_{\mathrm{c}} \cdot \dot{n}_{\mathrm{d,c}}. \tag{75}$$

Substances in the liquid phase will be dragged with the liquid,

$$\dot{n}_{\mathrm{H_2O}}^{\mathrm{d}} = x_{\mathrm{H_2O}}^{\mathrm{a}} \cdot \dot{n}_{\mathrm{d}} \tag{76}$$
$$\dot{n}_{\mathrm{H_2}}^{\mathrm{d}} = x_{\mathrm{H_2}}^{\mathrm{a}} \cdot \dot{n}_{\mathrm{d}} \tag{77}$$
$$\dot{n}_{\mathrm{O_2}}^{\mathrm{d}} = x_{\mathrm{O_2}}^{\mathrm{a}} \cdot \dot{n}_{\mathrm{d}} \tag{78}$$

In addition, hydrogen and oxygen in gas form will diffuse/permeate through the membrane with rates

$$\dot{n}_{\mathrm{H_2}}^{\delta} = N_{\mathrm{c}} \cdot \mathcal{P}_{\mathrm{H_2}} \frac{p_{\mathrm{H_2}}^{\mathrm{c}} - p_{\mathrm{H_2}}^{\mathrm{a}}}{\delta_{\mathrm{m}}} A_{\mathrm{m}} \tag{79}$$

$$\dot{n}_{\mathrm{O_2}}^{\delta} = N_{\mathrm{c}} \cdot \mathcal{P}_{\mathrm{O_2}} \frac{p_{\mathrm{O_2}}^{\mathrm{c}} - p_{\mathrm{O_2}}^{\mathrm{a}}}{\delta_{\mathrm{m}}} A_{\mathrm{m}}; \tag{80}$$

here, $\dot{n}_{\mathrm{H_2}}^{\delta}$ normally flows from the cathode side to the anode side, while $\dot{n}_{\mathrm{O_2}}^{\delta}$ flows from the anode side to the cathode side.

The circulating pumping rate $\dot{m}_{\mathrm{p}}^{\mathrm{a,c}}$ is only important if we consider energy balance; here, we will assume that T_{a} is fixed, and neglect the energy balance.

Gas leaves the anode separator through a valve in accordance with the simplified valve model in Section 3.4.2. Assuming a linear valve characteristic,

$$\frac{\dot{m}_{\mathrm{v}}^{\mathrm{a,e}}}{\dot{m}_{\mathrm{v}}^{\mathrm{a,c}}} = u_{\mathrm{v}}^{\mathrm{a}} \cdot Y_{\mathrm{a}} \cdot \sqrt{\frac{\Delta p_{\mathrm{a}}}{p^{\varsigma}} \cdot \frac{\rho_{\mathrm{i}}^{\mathrm{a}}}{\rho^{\varsigma}}} \tag{81}$$

where $u_{\mathrm{v}}^{\mathrm{a}} \in \{0, 1\}$ and with
$$\Delta p_{\mathrm{a}} = p_{\mathrm{a}} - p_{\mathrm{a}}^{\mathrm{e}}$$

$$Y = 1 - \min\left(1, \frac{2}{3} \frac{\Delta p_{\mathrm{a}}}{p_{\mathrm{a}}} \right).$$

For the mixture and $j \in \{H_2O, H_2, O_2\}$,

$$\rho_i^a = \frac{\sum_{j=1}^{N_s} y_j^a M_j}{\tilde{V}_g^a} \tag{82}$$

while

$$\dot{n}_j^{a,e} = y_j^a \cdot \dot{n}_v^{a,e} \tag{83}$$

where the molar valve rate is

$$\dot{n}_v^{a,e} = \frac{\dot{m}_v^{a,e}}{\sum_{j=1}^{N_s} y_j^a M_j} \tag{84}$$

Feed of pure water, $\dot{n}_{H_2O}^i$, can be considered an input, used to control the liquid level in the anode separator. To this end, with anode separator liquid volume V_ℓ^a, we can manipulate the influent liquid flow $\dot{n}_{H_2O}^i$ of fresh water, e.g., by using a simple P controller:

$$\dot{n}_{H_2O}^i = \dot{n}_{H_2O}^{i,ref} + K_p^a \left(V_\ell^{a,ref} - V_\ell^a \right). \tag{85}$$

Here, it is important to make sure that the resulting flow rate $\dot{n}_{H_2O}^i \geq 0$.

3.6. Cathode volume

With reference to Fig. 9, the cathode separator system can be depicted as in Fig. 11.

With N_c electrolysis cells in the electrolysis stack,

$$\dot{n}_{H_2}^g = N_c \cdot \frac{\nu_{H_2}}{\nu_{e^-}} \frac{A_m i''}{F}. \tag{86}$$

With known cathode separator amount vector $\mathbf{n}_c = \left(n_{H_2O}^c, n_{H_2}^c, n_{O_2}^c \right)$, cathode volume V_c, and cathode temperature T_c, VT flash as in Section 3.3 provides cathode mole fractions $x_c = \left(x_{H_2O}^c, x_{H_2}^c, x_{O_2}^c \right)$, $y_c = \left(y_{H_2O}^c, y_{H_2}^c, y_{O_2}^c \right)$, as well as cathode liquid and gas volumes V_ℓ^c and V_g^c, and cathode pressure p_c.

Water will be dragged through the membrane via proton (H^+) transport, as described in Section 3.5, Eq. 75, while the possible drag of oxygen and hydrogen are as in Eqs. 76, 77.

The pumping rate $\dot{m}_p^{c,c}$ is only important if we consider energy balance, and is not always used. Here, we will assume that $\dot{m}_p^{c,c} \equiv 0$. Gas leaves the cathode separator through a valve in accordance with the simplified valve model in Section 3.4.2. Assuming a linear valve characteristic,

$$\frac{\dot{m}_v^{c,e}}{\dot{m}_v^{c,c}} = u_v^c \cdot Y_c \cdot \sqrt{\frac{\Delta p_c}{p^\varsigma} \cdot \frac{\rho_i^c}{\rho^\varsigma}} \tag{87}$$

where $u_v^c \in \{0, 1\}$ and with

$$\Delta p_c = p_c - p_c^e$$

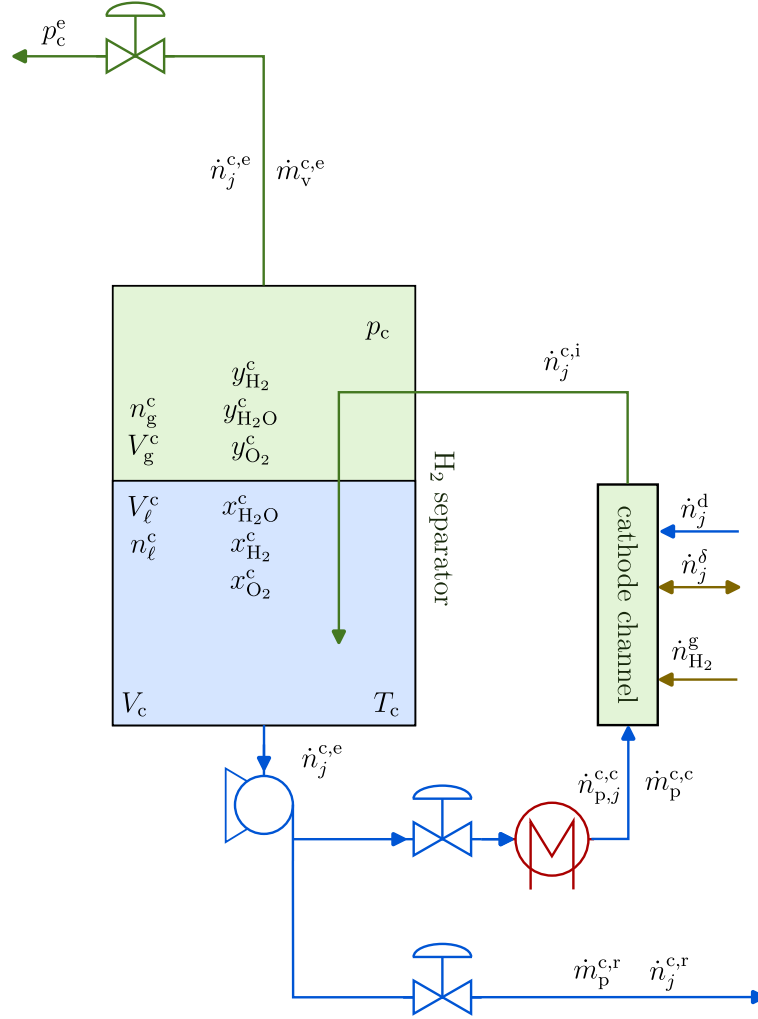$$Y = 1 - \min\left(1, \frac{2}{3} \frac{\Delta p_c}{p_c} \right).$$

Figure 11: Cathode separator subsystem.

For the mixture and $j \in \{H_2O, H_2, O_2\}$,

$$\rho_i^c = \frac{\sum_{j=1}^{N_s} y_j^c M_j}{\tilde{V}_g^c} \tag{88}$$

while

$$\dot{n}_j^{c,e} = y_j^c \cdot \dot{n}_v^{c,e} \tag{89}$$

where the molar valve rate is

$$\dot{n}_v^{c,e} = \frac{\dot{m}_v^{c,e}}{\sum_{j=1}^{N_s} y_j^c M_j}. \tag{90}$$

Recycled liquid flow rate $\dot{m}_p^{c,r}$ needs to be used to control the liquid level in the anode separator. To this end, with cathode separator liquid volume V_ℓ^c, we can manipulate $\dot{m}_p^{c,r}$, e.g., by using a simple P controller:

$$\dot{m}_p^{c,r} = \dot{m}_p^{c,r,ref} + K_p^c \left(V_\ell^c - V_\ell^{c,ref} \right). \tag{91}$$

Here, it is important to make sure that the resulting flow rate is constrained as $\dot{m}_p^{c,r} \geq 0$. With $\dot{m}_p^{c,r}$ computed, we can find the re-circulating liquid mixture molar flow rates as

$$\dot{n}_j^{c,r} = \frac{x_j^c}{\sum_{j=1}^{N_s} x_j^c M_j} \cdot \dot{m}_p^{c,r}. \tag{92}$$

4. Project tasks

4.1. Limiting the project scope

In this project, we will neglect temperature variation/energy balance. Thus, assume a temperature of $T = 60\,°C$ everywhere in the system. Some of the model parameters are given in non-SI units. Make sure that you correctly convert parameter values to compatible units to avoid errors. The simplest way to ensure compatible units is to use SI units, i.e., use mol instead of kmol, use kg instead of g, use J instead of kJ, use Pa instead of bar, etc. In most cases, temperature should be given in the absolute scale, i.e., K, but there may be expressions where temperature in °C is expected.

In a somewhat related project in course FM1015 in 2024, considerable emphasis was put on the electric subsystem of water electrolysis. Essentially, the electric subsystem gives a relationship between electrolyzer stack voltage u_s and current i or current density $i'' \triangleq i/A_m$ where A_m is the "superficial" membrane area; $i'' = f(u_s)$. The electric subsystem is important in that the stack voltage u_s is the real input variable used to manipulate the electrolyzer production of hydrogen and oxygen.

However, the non-electric parts of the electrolyzer model do not involve u_s, but only i or i''. It is possible to neglect the electric subsystem and only consider the current density i'' in the analysis of the electrolyzer. But for real world implementations, if i'' is computed, it is then necessary to solve an implicit equation $i'' = f(u_s)$ in order to find the stack voltage that must be applied to achieve i''.

Because the project in 2025 involves several extensions of the scope of the 2024 project, the electric subsystem will not be considered and we will assume that i'' can be chosen freely.

The problems are separated into two groups: steady state analysis, Section 4.2, and dynamic analysis, Section 4.3. In addition, there is a small section on uncertainty analysis.

Steady state analysis: Assume that the anode separator only consists of water and oxygen, and that the liquid phase is pure water. Similarly, assume that the cathode separator only consists of water and hydrogen, and that the liquid phase is pure water. This provides a simple way to find approximate steady state values of $n_{H_2O}^a$, $n_{O_2}^a$, $n_{H_2O}^c$, and $n_{H_2}^c$.

Next, assume that the light gases (oxygen, hydrogen) dominate in the gas phase, so that $\dot{n}_{O_2}^{a,e} \approx \frac{\dot{m}_v^{a,e}}{M_{O_2}}$ and $\dot{n}_{H_2}^{c,e} \approx \frac{\dot{m}_v^{c,e}}{M_{H_2}}$. These two approximations make it possible to compute approximate steady state values for $\dot{m}_v^{a,e}$ and $\dot{m}_v^{c,e}$. Then choose, say, $u_v = 0.5$, and compute valve capacities $\dot{m}_v^{a,e,c}$ and $\dot{m}_v^{c,e,c}$.

Dynamic analysis: With the steady state values as well as valve and controller reference values found in the steady state analysis, the steady state values can be chosen as initial values in simulation of the dynamic system. Because some approximations have been used, the dynamic system will then not start entirely in steady state.

4.2. Steady state analysis

Chemical reaction

The overall reaction is given as

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2. \tag{93}$$

Problem 1. Overall stoichiometric coefficients.

With the overall reaction in Eq. 93,

- Give the stoichiometric coefficients ν for the overall reaction, as well as the (hidden) stoichiometric coefficient for electrons, ν_{e^-}. (**Hint**: Example 3, p. 12.) ▲

Steady separator tank amounts

Problem 2. Water amount in separator systems.

For simplicity, assume that the separator tanks are one third full (33%) with liquid water. Use parameters in Tables 5, 6 of Appendix A.

- Find the amount (mole) of liquid water (H_2O) in the anode separator tank, $n_{H_2O}^a$.

- Find the amount (mole) of liquid water (H_2O) in the cathode separator tank, $n_{H_2O}^c$. ▲

Problem 3. Gas amounts in separator systems.

- Find the corresponding saturation pressure of water in the two tanks, $p_{H_2O}^{sat}$.

Assume pressures $p_a = 1.2\,\text{bar}$ and $p_c = 30\,\text{bar}$.

- Find the partial pressure of oxygen in the anode separator tank, $p_{O_2}^a$, and the corresponding amount (mole) of oxygen in this tank, $n_{O_2}^a$. Assume that the amount of hydrogen is zero, $n_{H_2}^a = 0$ (this will change in dynamic simulations).

- Find the partial pressure of hydrogen in the cathode separator tank, $p_{H_2}^c$, and the corresponding amount (mole) of hydrogen in this tank, $n_{H_2}^c$. Assume that the amount of oxygen is zero, $n_{O_2}^c = 0$. ▲

Steady water flows

Problem 4. Water consumption in electrolyzer. Water circulation through anode channel.

With parameters from Tables 5, 6 of Appendix A and results found previously, assume that the current density is $i'' = 2\,\text{A/cm}^2$,

- Find the water generation $\dot{n}_{\text{H}_2\text{O}}^{\text{g}}$ and corresponding water consumption: the consumption will be approximately equal to the necessary feed of fresh water to the system, see $\dot{n}_{\text{H}_2\text{O}}^{\text{i}}$ in Fig. 10 (assuming that water dragged through the membrane is returned to the anode separator tank). ▲

Problem 5. Water flow through membrane.

With parameters from Tables 5, 6 of Appendix A and results found previously, assume that $i'' = 2\,\text{A/cm}^2$,

- Find the water flow dragged through the membrane, $\dot{n}_{\text{H}_2\text{O}}^{\text{d}}$.

- Find the mass flow rate $\dot{m}_{\text{H}_2\text{O}}^{\text{d}}$, which will be approximately the flow that should leave the cathode tank via $\dot{m}_{\text{p}}^{\text{c,r}}$. ▲

Steady gas flows

Problem 6. Gas production in electrolyzer.

With parameters from Tables 5, 6 of Appendix A and results found previously, assume that $i'' = 2\,\text{A/cm}^2$,

- Find the corresponding oxygen production $\dot{n}_{\text{O}_2}^{\text{g}}$.

- Find the corresponding hydrogen production $\dot{n}_{\text{H}_2}^{\text{g}}$. ▲

Problem 7. Oxygen flow to ambient.

With parameters from Tables 5, 6 of Appendix A and results found previously,

- Find the corresponding oxygen effluent $\dot{n}_{\text{O}_2}^{\text{a,e}}$.

- Find the corresponding mass flow $\dot{m}_{\text{O}_2}^{\text{a,e}}$ to the atmosphere, and use $\dot{m}_{\text{v}}^{\text{a,e}} \approx \dot{m}_{\text{O}_2}^{\text{a,e}}$.

- Set, e.g., $u_{\text{v}}^{\text{a}} = 0.5$, and find a corresponding valve capacity $\dot{m}_{\text{v}}^{\text{a,e,c}}$. ▲

Problem 8. Hydrogen flow to storage tank.

With parameters from Tables 5, 6 of Appendix A and results found previously,

- Find the corresponding hydrogen effluent $\dot{n}_{\text{H}_2}^{\text{c,e}}$.

- Find the corresponding mass flow $\dot{m}_{\text{H}_2}^{\text{c,e}}$ to the storage tank, and use $\dot{m}_{\text{v}}^{\text{c,e}} \approx \dot{m}_{\text{H}_2}^{\text{c,e}}$.

- Set, e.g., $u_{\text{v}}^{\text{c}} = 0.5$, and find a corresponding valve capacity $\dot{m}_{\text{v}}^{\text{c,e,c}}$. ▲
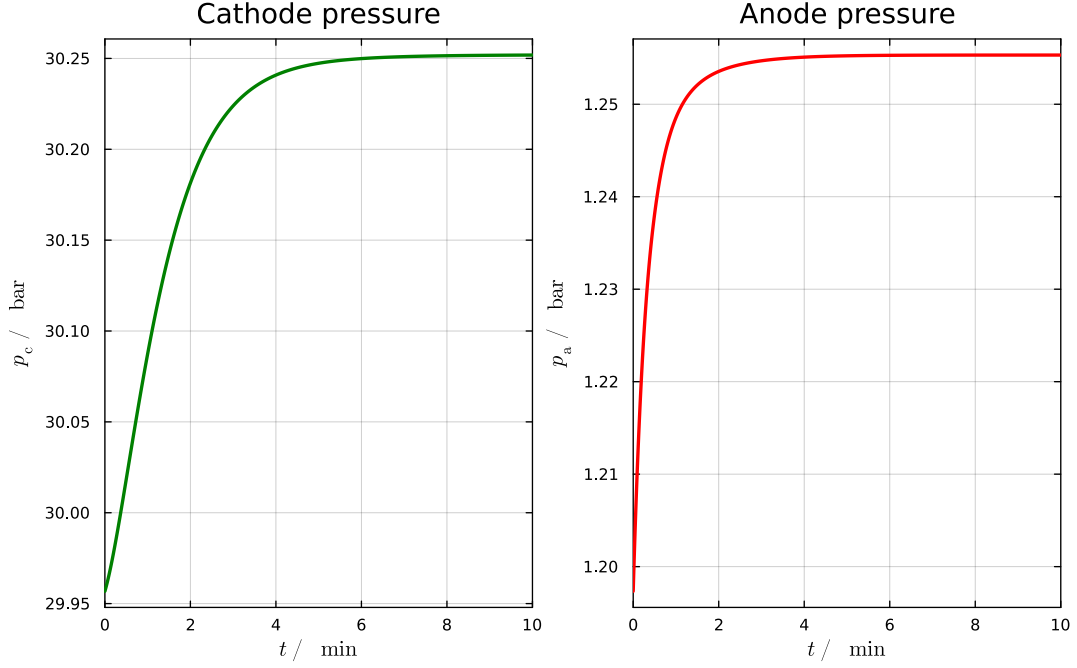
Figure 12: Pressure evolution in cathode and anode separators.

4.3. Dynamic analysis

Electrolyzers are fed (liquid) water H_2O, and by applying an external stack voltage u_s over the electrolyzer stack, water is converted into hydrogen H_2 and oxygen O_2. All generation rates (consumption of water, production of hydrogen, oxygen) are directly proportional to the *current i*, or rather: current density i'' going through the cells in the stack. Here, we should use i'' as input, and neglect the electric subsystem.

With parameters and operating conditions from Appendices A–B, Figure 12 indicates the pressure evolution in the anode and the cathode separators.

No problem is seen in Fig. 12, but flow through valves will create simulation crash if the computed pressure drop Δp across the valve becomes negative. A simple trick around this problem is to replace Δp in the valve model with $\max(0, \Delta p)$, which will effectively make the valve a one-way valve where reversed flow rate is blocked.

Figure 13 indicates the evolution of liquid volume fractions in the anode and cathode separators. Note that the P-controllers try to make these fractions equal to 1/3 (but: with P control, there is always some steady state deviation).

Figure 14 indicates the evolution of controlled molar flow rates $\dot{n}^i_{H_2O}$ and $\dot{n}^{cr}_p$. Observe that it is a good idea to use a `max(0,nd)`[24] function on the computed molar flow rate `nd` to avoid that the flow rate is reversed; reversed flow rates leads to all sorts of problems.

In Fig. 14, the effect of using the `max(0,nd)` can be seen in the response in $\dot{n}^i_{H_2O}$ — without this max-function, water would have been *sucked out* of the anode volume initially, which is not what we want.

Figure 15 indicates the evolution of the hydrogen-to-oxygen mole fraction ratio (in %) in the anode gas volume. If the fraction of hydrogen is in the range 4-95% *by volume*, the mixture is "flammable" and may detonate/explode. If we assume ideal gas, the volume

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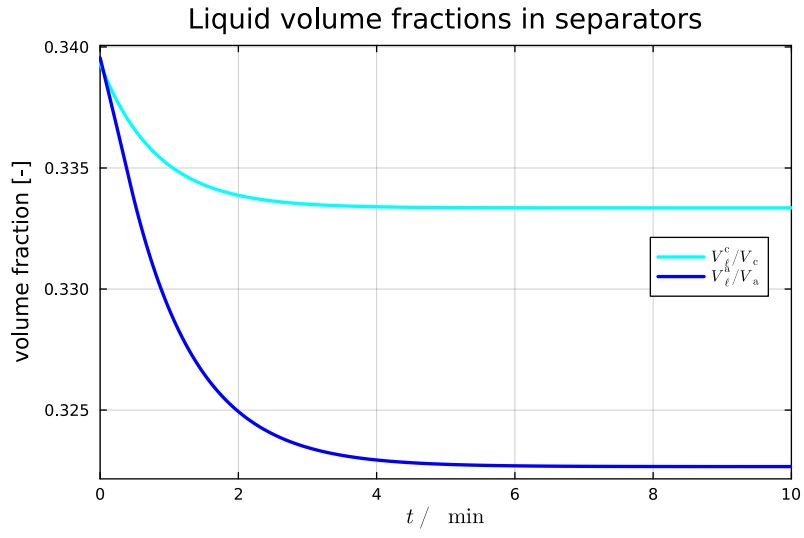[24]`nd` is my syntax for $\dot{n}$ — "n with a dot"

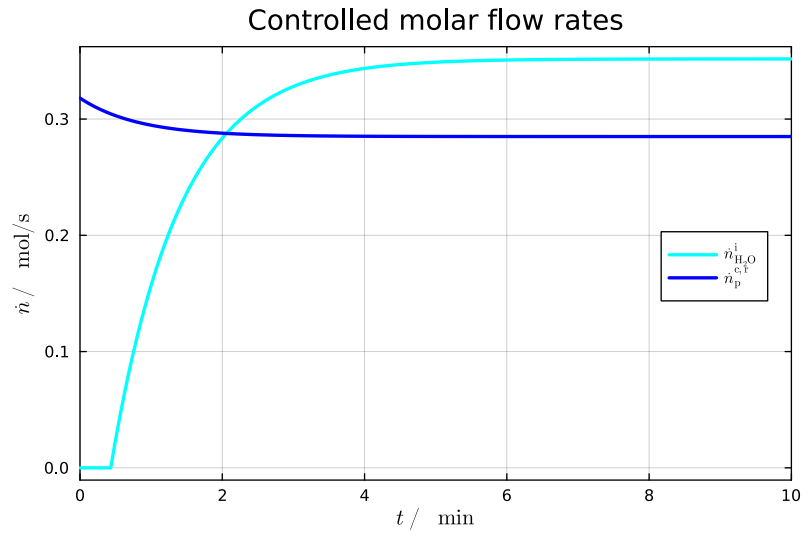Figure 13: Liquid volume fraction evolution in the anode and cathode separators.

Figure 14: Controlled molar flow rates in the system.
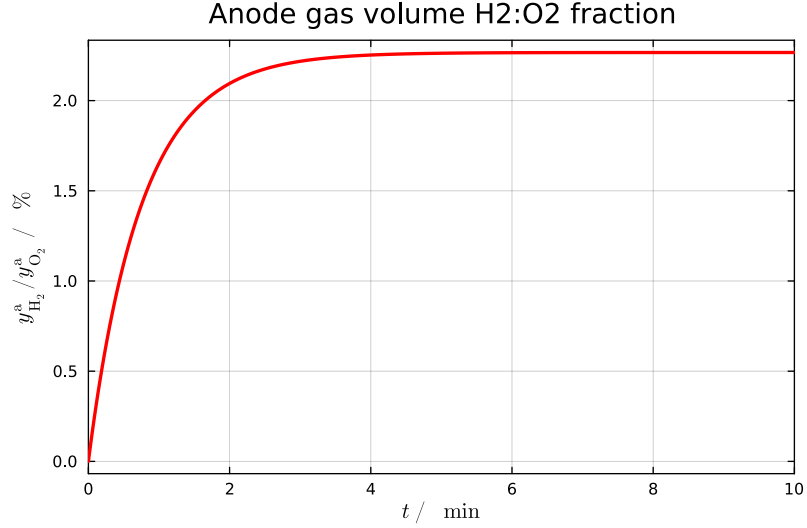
Figure 15: Hydrogen-to-oxygen mole fraction ratio (%) in anode gas.
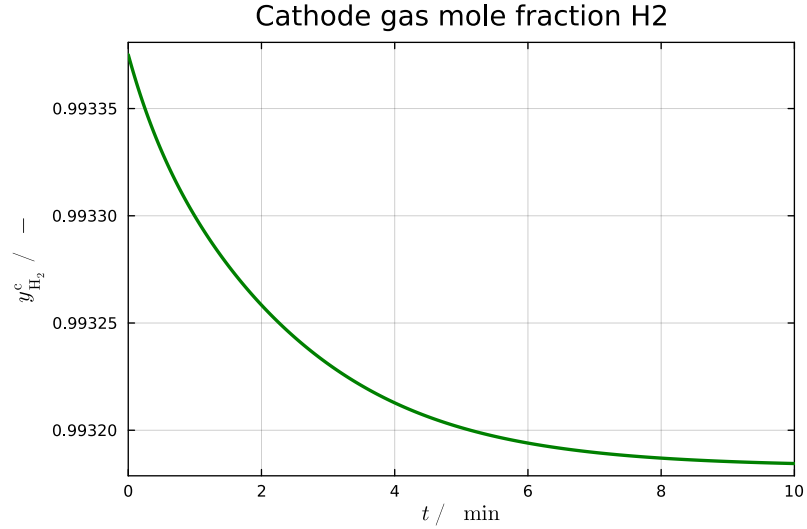
Figure 16: Controlled molar flow rates in the system.

fraction equals the mole fraction ratio.

Figure 16 indicates the evolution of the hydrogen mole fraction in the cathode gas volume. Fraction $y_{H_2}^c$ must be high to produce as pure hydrogen as possible.

Problem 9. Dynamic model of electrolyzer stack.

Consider the electrolyzer stack with current density i'' is the input.

- For the electrolyzer system, develop mole balances for the three substances H_2O, H_2, and O_2 in both separator volumes, i.e., for n_j^a and n_j^c where $j \in \{H_2O, H_2, O_2\}$ where you include all the generation/flow terms indicated in Table 3. Include the appropriate flash computations as well as transport equipment models (valves, pumps) needed, and level controllers. ▲

In the subsequent implementation and simulation of the model, an important part of the model implementation is VT flash. To aid in debugging of your code, if the inputs to the

flash algorithm are

$$V_\mathrm{a} = 30\,\mathrm{L}$$
$$T_\mathrm{a} = 60\,^\circ\mathrm{C}$$
$$\mathbf{n} = (n_{\mathrm{H_2O}}, n_{\mathrm{H_2}}, n_{\mathrm{O_2}}) = (556, 0, 0.7224)$$

then the output from the VT flash should be

$$x_\mathrm{a} = \left(x^\mathrm{a}_{\mathrm{H_2O}}, x^\mathrm{a}_{\mathrm{H_2}}, x^\mathrm{a}_{\mathrm{O_2}}\right) \approx \left(0.999984, 0, 1.5588 \cdot 10^{-5}\right)$$
$$y_\mathrm{a} = \left(y^\mathrm{a}_{\mathrm{H_2O}}, y^\mathrm{a}_{\mathrm{H_2}}, y^\mathrm{a}_{\mathrm{O_2}}\right) \approx (0.16589, 0, 0.83411)$$
$$n^\mathrm{a}_\ell \approx 555.87\,\mathrm{mol}$$
$$n^\mathrm{a}_\mathrm{g} \approx 0.85569\,\mathrm{mol}$$
$$\tilde{V}^\mathrm{a}_\ell \approx 1.8326 \cdot 10^{-5}\,\mathrm{m^3/mol}$$
$$\tilde{V}^\mathrm{a}_\mathrm{g} \approx 0.02315\,\mathrm{m^3/mol}$$
$$p_\mathrm{a} \approx 1.19732 \cdot 10^5\,\mathrm{Pa}.$$

Problem 10. Simulation of electrolyzer stack.

Consider the model developed in Problem 9, with i'' as the input.

- Implement the developed model in a simulation tool, and use model parameters as found in Appendix A. As initial values for states, use steady state values found in Problems 2–3 for $\dot{n}^\mathrm{a}_{\mathrm{H_2O}}$, $\dot{n}^\mathrm{a}_{\mathrm{O_2}}$, $\dot{n}^\mathrm{c}_{\mathrm{H_2O}}$, and $\dot{n}^\mathrm{c}_{\mathrm{H_2}}$, and set $\dot{n}^\mathrm{a}_{\mathrm{H_2}}(t=0) = 0$ and $\dot{n}^\mathrm{c}_{\mathrm{O_2}}(t=0) = 0$. At first, use constant inputs ($i'' = 2\,\mathrm{A/cm^2}$, etc.) to test your simulations.

- Next, use the inputs as indicated in Appendix B. Demonstrate that you find similar evolution of pressures as in Figs. 12 and 13.

- Which transport mechanisms of hydrogen and oxygen appear to be most important for the distribution of hydrogen to the anode tank and oxygen to the cathode tank?

- Experiment with the model wrt. different changes in i'', temperature T, and downstream hydrogen pressure p^e_c.

- Suggest time constants for the system. ▲

4.4. Model uncertainty

The model is not perfect.

Problem 11. Parameter uncertainty.

- Choose 2 parameters, and see what happens if you vary the parameters randomly in a certain range around the nominal values provided in Appendix A. (E.g., proportional gains in the level controllers, K^a_p, K^a_p, drag coefficient η_d, etc.).

- Report your findings. ▲

Table 5: Thermodynamic data relevant for water electrolysis cell. Antoine model data from Poling et al. (2001).

Parameter	Value	Description
R	$8.314\,\mathrm{J/mol\,K}$	Ideal gas constant
F	$9.648 \cdot 10^4\,\mathrm{C/mol}$	Faraday's constant
ν	Problem 1	Stoichiometric matrix for species vector S = (H_2O, H_2, O_2)
ν_{e^-}	Problem 1	"Hidden" electron stoichiometric coefficient
$\rho_{\mathrm{H_2O}}$	$1\,\mathrm{kg/L}$	Density of water
$M_{\mathrm{H_2O}}$	$18\,\mathrm{g/mol}$	Molar mass, H_2O
$M_{\mathrm{H_2}}$	$2\,\mathrm{g/mol}$	Molar mass, H_2
$M_{\mathrm{O_2}}$	$32\,\mathrm{g/mol}$	Molar mass, O_2
$A_{\mathrm{H_2O}}$	$5.11564 -$	Antoine correlation, valid $[273.20, 473.20]\,\mathrm{K} \times [10^{-2}, 16]\,\mathrm{bar}$
$B_{\mathrm{H_2O}}$	$1687.537\,\mathrm{K}$	Antoine correlation, valid $[273.20, 473.20]\,\mathrm{K} \times [10^{-2}, 16]\,\mathrm{bar}$
$C_{\mathrm{H_2O}}$	$230.17\,\mathrm{K}$	Antoine correlation, valid $[273.20, 473.20]\,\mathrm{K} \times [10^{-2}, 16]\,\mathrm{bar}$
$\mathcal{P}_{\mathrm{H_2}}$	$5.31 \cdot 10^{-14}\,\mathrm{mol/s\,m\,Pa}$	Membrane hydrogen permeability
$\mathcal{P}_{\mathrm{O_2}}$	$2.26 \cdot 10^{-14}\,\mathrm{mol/s\,m\,Pa}$	Membrane oxygen permeability
$T_{\mathrm{c}}^{\mathrm{H_2O}}$	$641.7\,\mathrm{K}$	Water critical temperature
$\mathcal{H}_{\max}^{\mathrm{H_2}}$	$7.54 \cdot 10^4\,\mathrm{atm}$	Hydrogen maximum Henry constant
$\frac{1}{T_{\max}^{\mathrm{H_2}}}$	$3.09 \cdot 10^{-3}\,\mathrm{1/K}$	Hydrogen inverse maximum temperature
$T_{\mathrm{c}}^{\mathrm{H_2}}$	$33.2\,\mathrm{K}$	Hydrogen critical temperature
$\mathcal{H}_{\max}^{\mathrm{O_2}}$	$7.08 \cdot 10^4\,\mathrm{atm}$	Oxygen maximum Henry constant
$\frac{1}{T_{\max}^{\mathrm{O_2}}}$	$2.73 \cdot 10^{-3}\,\mathrm{1/K}$	Oxygen inverse maximum temperature
$T_{\mathrm{c}}^{\mathrm{O_2}}$	$154.6\,\mathrm{K}$	Oxygen critical temperature

4.5. Documentation

Write a partial report and submit it in the Canvas group folder within the deadline. Write a technical report on the project and results (single file, maximum 15 pages + 1 cover page, PDF format) and submit the report in the Canvas group folder within the deadline. Prepare a "PowerPoint" presentation (= use PowerPoint or other tools) of 7 min for the oral presentation.

A. Electrolyzer Parameters

Parameters for a Water Electrolyzer are given in Tables 5–6.

First, consider general thermodynamic parameters relevant for the electrolyzer cell, Table 5.

Electrolyzer cell and stack parameters are given in Table 6.

Table 6: Electrolyzer cell and stack parameters.

Parameter	Value	Description
A_{m}	$90\,\mathrm{cm^2}$	Superficial membrane area
δ_{m}	$200\,\mu\mathrm{m}$	Membrane thickness
N_{c}	34	Number of electrolyzer cells in stack
V_{a}	$30\,\mathrm{L}$	Anode separator volume
V_{c}	$5\,\mathrm{L}$	Cathode separator volume
$V_{\ell}^{\mathrm{a,ref}}$	$V_{\mathrm{a}}/3$	Liquid water reference volume, anode separator
$V_{\ell}^{\mathrm{c,ref}}$	$V_{\mathrm{c}}/3$	Liquid water reference volume, cathode separator
p^{ς}	$1\,\mathrm{bar}$	Scaling pressure for valve model
ρ^{ς}	$1\,\mathrm{kg/m^3}$	Scaling (gas) density for valve model
$\dot{m}_{\mathrm{v}}^{\mathrm{a,e,c}}$	Problem 7	Valve capacity, anode effluent gas flow.
$\dot{m}_{\mathrm{v}}^{\mathrm{c,e,c}}$	Problem 8	Valve capacity, cathode effluent gas flow.
$\dot{n}_{\mathrm{H_2O}}^{\mathrm{i,ref}}$	$\approx \dot{n}_{\mathrm{H_2O}}^{\mathrm{g}}$, Problem 4	Reference fresh water influent for P-controller of anode liquid volume.
$\dot{m}_{\mathrm{p}}^{\mathrm{c,r,ref}}$	$\approx \dot{m}_{\mathrm{H_2O}}^{\mathrm{d}}$, Problem 5	Reference pump flow for P-controller of cathode liquid volume.
$K_{\mathrm{p}}^{\mathrm{a}}$	10^3	Anode separator proportional controller gain
$K_{\mathrm{p}}^{\mathrm{c}}$	20	Cathode separator proportional controller gain

Table 7: Operating conditions for the Electrolyzer system.

Variable	Value	Description
$n_{H_2O}^{a}(0)$	Problem 2	Initial amount of H_2O in anode separator.
$n_{H_2}^{a}(0)$	0	Initial amount of H_2 in anode separator.
$n_{O_2}^{a}(0)$	Problem 3	Initial amount of O_2 in anode separator.
$n_{H_2O}^{c}(0)$	Problem 2	Initial amount of H_2O in cathode separator.
$n_{H_2}^{c}(0)$	Problem 3	Initial amount of H_2 in cathode separator.
$n_{O_2}^{c}(0)$	0	Initial amount of O_2 in cathode separator.
T	$60 + 273.15\,\mathrm{K}$	Default operating temperature
i''	$2\,\mathrm{A/cm^2}$	Default current density
p_a^e	$1\,\mathrm{bar}$	Default external pressure for gas flow from anode
p_c^e	$25\,\mathrm{bar}$	Default external pressure for gas flow from cathode
$\dot{n}_p^{a,c}$	$0\,\mathrm{mol/s}$	Default pumped circulation molar rate in anode tank
$\dot{n}_p^{c,c}$	$0\,\mathrm{mol/s}$	Default pumped circulation molar rate in cathode tank
u_v^a	$0\,-$	Default anode gas valve control signal
u_v^c	$0\,-$	Default cathode gas valve control signal
i''	$2 - \mathbb{H}_{5\min}(t)\,,\mathrm{A/cm^2}$	Possible step in current density. Heaviside function $\mathbb{H}_\tau(t) = \begin{cases} 0, & t < \tau \\ 1, & t \geq \tau \end{cases}$
p_c^e	$25 - 0.5 \cdot \mathbb{H}_{10\min}(t)\,,\mathrm{bar}$	Possible step in cathode-external pressure.
T	$60 + 5 \cdot \mathbb{H}_{15\min}(t)\,,^\circ\mathrm{C}$	Possible step in stack temperature.

B. Electrolyzer Operating Conditions

Initial state and nominal input values are indicated in Table 7.

References

Abdol Rahim, A. H., Tijani, A. S., Kamarudin, S. K. & Hanapi, S. (2016), 'An overview of polymer electrolyte membrane electrolyzer for hydrogen production: Modeling and mass transport', *Journal of Power Sources* **309**, 56–65.

Cavaliere, P. (2023), *Water Electrolysis for Hydrogen Production*, Springer.

Crespi, E., Guandalini, G., Mastropasqua, L., Campanari, S. & Brouwer, J. (2023), 'Experimental and theoretical evaluation of a 60 kW PEM electrolysis system for flexible dynamic operation', *Energy Conversion and Management* **277**, 116622.

Datta, R., Martino, D., Dong, Y. & Choi, P. (2015), Modeling of PEM Water Electrolyzer: Principles and Applications, pp. 243–267.

Dickinson, E. J. E. & Smith, G. (2020), 'Modelling the Proton-Conductive Membrane in

Practical Polymer Electrolyte Membrane Fuel Cell (PEMFC) Simulation: A Review', *Membranes* **10**(11), 310.

Dicks, A. L. & Rand, D. A. (2018), *Fuel Cell Systems Explained*, 3rd edn, John Wiley & Sons Ltd., Hoboken, NJ.

Dutta, S., Shimpalee, S. & Van Zee, J. W. (2001), 'Numerical prediction of mass-exchange between cathode and anode channels in a PEM fuel cell', *International Journal of Heat and Mass Transfer* **44**(11), 2029–2042.

Eikerling, M., Kharkats, Y. I., Kornyshev, A. A. & Volfkovich, Y. M. (1998), 'Phenomenological Theory of Electro-osmotic Effect and Water Management in Polymer Electrolyte Proton-Conducting Membranes', *Journal of The Electrochemical Society* **145**(8), 2684.

Fuller, T. F. & Harb, J. N. (2018), *Electrochemical Engineering*, John Wiley & Sons, Hoboken, NJ.

Görgün, H. (2006), 'Dynamic modelling of a proton exchange membrane (PEM) electrolyzer', *International Journal of Hydrogen Energy* **31**(1), 29–38.

Himmelblau, D. M. (1960), 'Solubilities of Inert Gases in Water. 0° C. to Near the Critical Point of Water.', *Journal of Chemical & Engineering Data* **5**(1), 10–15.

Holst, M., Aschbrenner, S., Smolinka, T., Voglstätter, C. & Grimm, G. (2021), 'Cost Forecast for Low Temperature Electrolysis - Technology Driven Bottom-Up Prognosis for PEM and Alkaline Water Electrolysis Systems'.

Ito, H., Maeda, T., Nakano, A., Hasegawa, Y., Yokoi, N., Hwang, C. M., Ishida, M., Kato, A. & Yoshida, T. (2010), 'Effect of flow regime of circulating water on a proton exchange membrane electrolyzer', *International Journal of Hydrogen Energy* **35**(18), 9550–9560.

Ito, H., Maeda, T., Nakano, A. & Takenaka, H. (2011), 'Properties of Nafion membranes under PEM water electrolysis conditions', *International Journal of Hydrogen Energy* **36**(17), 10527–10540.

Mann, R. F., Amphlett, J. C., Hooper, M. A. I., Jensen, H. M., Peppley, B. A. & Roberge, P. R. (2000), 'Development and application of a generalised steady-state electrochemical model for a PEM fuel cell', *Journal of Power Sources* **86**, 173–180.

Marangio, F., Santarelli, M. & Calì, M. (2009), 'Theoretical model and experimental analysis of a high pressure PEM water electrolyser for hydrogen production', *International Journal of Hydrogen Energy* **34**(3), 1143–1158.

Olivier, P., Bourasseau, C. & Bouamama, B. (2017), 'Dynamic and multiphysic PEM electrolysis system modelling: A bond graph approach', *International Journal of Hydrogen Energy* **42**(22), 14872–14904.

Onda, K., Murakami, T., Hikosaka, T., Kobayashi, M., Notu, R. & Ito, K. (2002), 'Performance Analysis of Polymer-Electrolyte Water Electrolysis Cell at a Small-Unit Test Cell and Performance Prediction of Large Stacked Cell', *Journal of The Electrochemical Society* **149**(8), A1069.

Pettersen, T., Cossar, E., Bergstrøm, T. H., Raka, Y. D., Lee, S. & Zenith, F. (2024), 'Simulation study on preventing explosive mixture formation in PEM electrolysers' water recovery tanks', *International Journal of Hydrogen Energy* **84**, 1021–1032.

Poling, B. E., Prausnitz, J. M. & O'Connell, J. P. (2001), *The Properties of Gases and Liquids*, 5th edn, McGraw-Hill, Boston.

Schalenbach, M. (2016), 'Corrigendum to "Pressurized PEM water electrolysis: Efficiency and gas crossover"', *International Journal of Hydrogen Energy* **41**, 729–732.

Schalenbach, M., Carmo, M., Fritz, D. L., Mergel, J. & Stolten, D. (2013), 'Pressurized PEM water electrolysis: Efficiency and gas crossover', *International Journal of Hydrogen Energy* **38**(35), 14921–14933.

Springer, T. E., Zawodzinski, T. A. & Gottesfeld, S. (1991), 'Polymer Electrolyte Fuel Cell Model', *Journal of The Elecrochemical Society* **138**(8), 2334–2342.

Suermann, M., Pătru, A., Schmidt, T. J. & Büchi, F. N. (2017), 'High pressure polymer electrolyte water electrolysis: Test bench development and electrochemical analysis', *International Journal of Hydrogen Energy* **42**(17), 12076–12086.

Thampan, T., Malhotra, S., Zhang, J. & Datta, R. (2001), 'PEM fuel cell as a membrane reactor', *Catalysis Today* **67**(1), 15–32.