# University of South-Eastern Norway

# Examination Information Page
### Written examination

## General information about the exam:

**Subject code: FM1015**

**Subject name: Modelling of Dynamic Systems**

**Examination date: 29.11.2024**

**Examination time: 09:00-12:00**

**Total hours: 3**

**Responsible course manager: Bernt Lie**

**Campus:** Porsgrunn

**Faculty: Technology, Natural Sciences and Maritime Sciences**

**No. of assignments: 20 Problems (= questions)**

**No. of attachments:  1**

**No. of pages incl. information page and attachments: front pages + 20 (1-21)**

## Permitted aids (cf. course plan):

No documents in printed or electronic form are allowed, no use of internet search allowed. Use of computer computation tools such as Python, Julia, or MATLAB are allowed

## Information regarding attachments:

Multiple Choice exam: insert answers (A-D) in attached Excel sheet, and upload in Excel file format.

## Comments:

Multiple Choice exam: insert answers (A-D) in attached Excel sheet, and upload in Excel file format.

## Exam assignment:

Each of 20 Problems has optional answers A, B, C, D. Make your choice of A-D.

If the exam isn't in digital form, please select the type of examination paper:
 Spreadsheets ☐ Line sheets ☐

**THE CANDIDATE MUST VERIFY THAT THE TASK SET IS COMPLETE ON THEIR OWN.**

# Exam: FM1015 Modelling of Dynamic Systems

## Date: Friday, November 29, 2024

*Form of exam:* This is a *Digital Exam* of type *Multiple* Choice. Each exam *question* (denoted "problems" in the text below) is followed by *4 possible answers* ("choice" in the tables related to questions). *Some* details about your answers and how they will be assessed:

- A problem gives full score if a correct and no incorrect choices are given, zero score otherwise.

- All problems are given the same weight.

- Most problems are posed so that it is necessary to do background development/calculations on paper to choose the correct answer (A–D).

- The background calculations shall not be submitted — the only submission in the Digital Exam are the choices (A–D) in each problem.

    - You need to insert the answers in the *attached* Excel sheet, and upload this Excel sheet which includes your answers, in the exam system [WISEflow].

    - The file you **upload must be in Excel file format**, i.e., *.xlsx format. (*Reason*: the files will be automatically parsed for grading. This parsing doesn't work if you upload a *.pdf file or any other file format.)

- A total score of 0-39% gives grade F (fail), score 40-49% gives grade E, score 50-59% gives grade D, score 60-79% gives grade C, score 80-89% gives grade B, and score 90-100% gives grade A.

*Aids*: No documents in printed or electronic form are allowed, no use of internet search allowed. Use of computer computation tools such as Python, Julia, or MATLAB are allowed. Necessary use of PC for using WISEflow, and the use of Excel for filling in answers is allowed.

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This exam contains questions (denoted *problems*) in the *Problems* part. The Problems part consists of *20 problems*, each with 4 alternative choices (A–D), spread over 7 subsections.

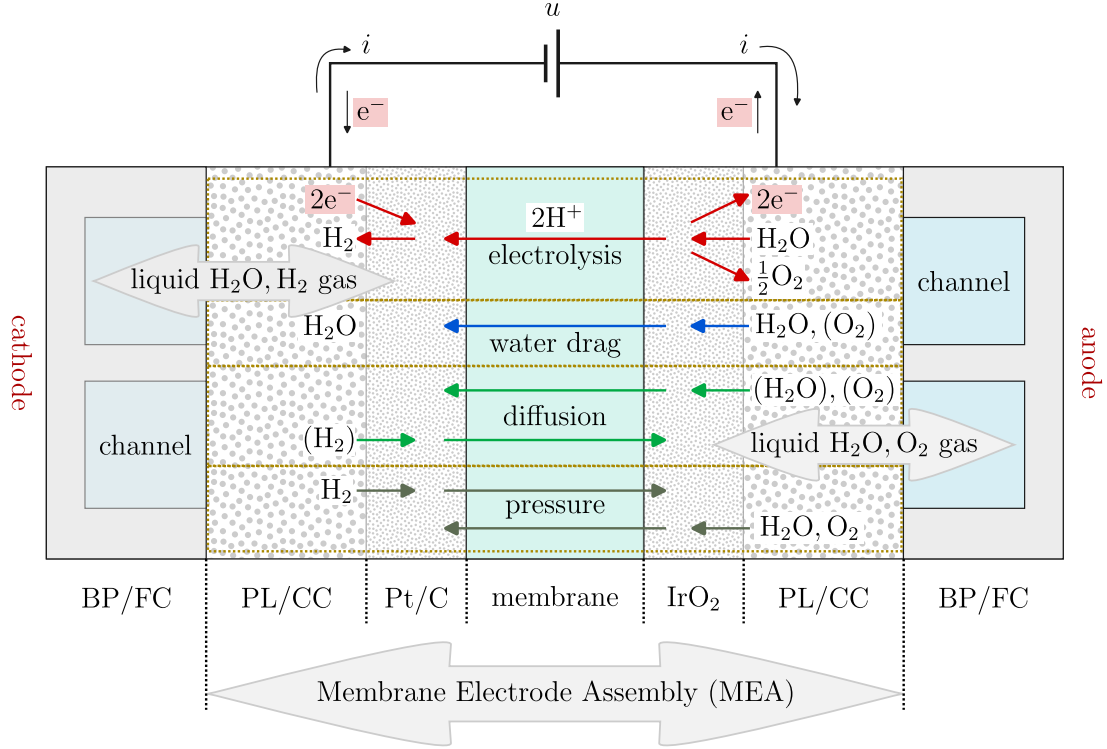| Contact person for questions during the exam: | |
|---|---|
| Name: | Bernt Lie |
| Phone: | 41 80 77 44 |
| Room: | B-257b |

Figure 1: PEM Electrolysis Cell, with (left-to-right) indication of *cathode* side Bipolar Plate with Flow Channel (BP/FC), 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.

# 1    Problems

In water electrolysis, water ($H_2O$) is split into hydrogen ($H_2$) and oxygen ($O_2$) by providing electric power. Because hydrogen and oxygen form an explosive mixture if mixed, a membrane is used to separate the generated hydrogen and oxygen.

Hydrogen is stored at high pressure. The produced hydrogen can either be compressed up to the storage pressure (relatively expensive), or produced at the required pressure in the electrolyzer. This means that it may be advantageous to keep the hydrogen side of the electrolyzer close to the storage pressure.

In this exam, we consider a water electrolysis cell separating the produced hydrogen and oxygen by a Proton Exchange Membrane (PEM), see Fig. 1.

The surrounding infrastructure of a stack of PEM electrolyzer cells is depicted in Fig. 2.

Details of the PEM electrolysis system in Fig. 2 were studied in the compulsory student group project in 2024. With the group project in mind, consider the following problems — which have been organized under numbered sub-headings.

## 1.1    Stoichiometry

Consider an electrolyzer where water ($H_2O$) is available at the *anode* surface, and a voltage is set up across an acidic electrolyte membrane [PEM: proton exchange membrane,
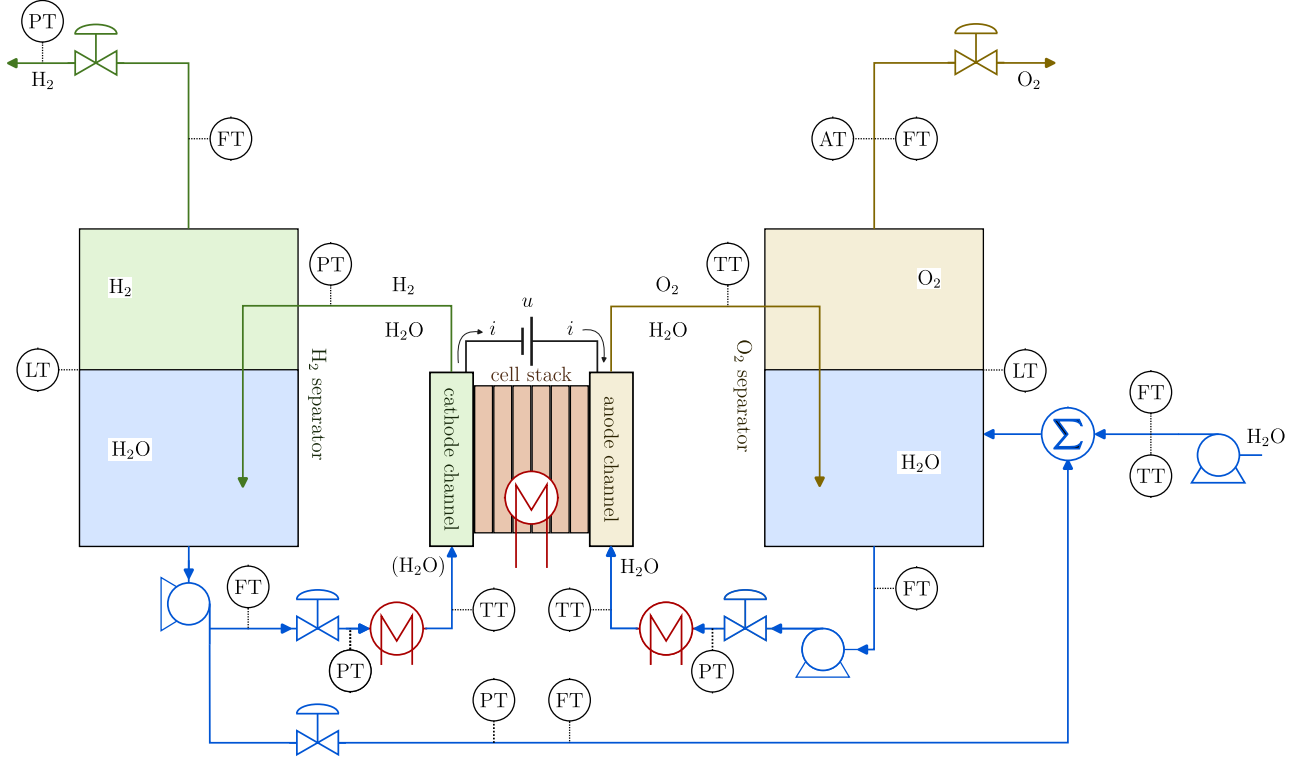
Figure 2: PEM Electrolysis System.

allowing for transport of *proton* ($H^+$) through the membrane]. This membrane separates the anode surface/volume from the cathode surface/volume, see Figs. 1 and 3.

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

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

With an acidic membrane, the catalyzed half-cell reaction at the anode surface produces oxygen [Oxygen Evolution Reaction, OER], while catalyzed half-cell reaction at the cathode surface produces hydrogen [Hydrogen Evolution Reaction, HER].

The overall half-cell reactions[1] are the anode (OER) half-cell reaction

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

and the cathode (HER) half-cell reaction

$$2H^+ + 2e^- \rightarrow H_2. \tag{3}$$

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 (as in a PEM cell), water must be available on the anode side.

**Problem 1.** Reactions in Electrolyzer

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[1]"overall half-cell reactions": the real reactions are much more complex, so the listed half-cell reactions are the overall reactions at the half-cells.
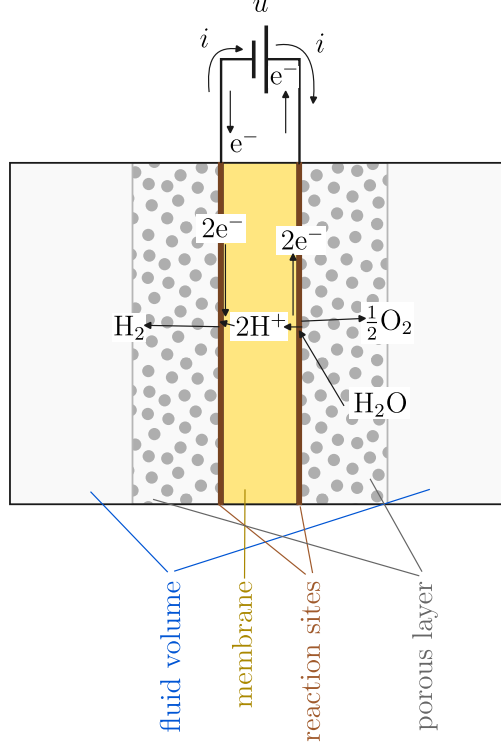
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Figure 3: Principle of water electrolysis with acidic membrane.

Let the species be ordered according to the vector $(H_2O, H_2, O_2)$. It is of interest to formulate the *stoichiometric matrix* $\nu$ [possibly a row matrix/vector] for the overall reaction in Eq. 1, as well as the *positive stoichiometric parameter* for the *electron*, $\nu_{e-}$ (Note: $\nu_{e-} > 0$).

| | **Problem 1:** Which of the following pairs of $\nu$ and $\nu_{e-}$ is ***incorrect?*** | Choice |
|---|---|---|
| A: | $\nu = \left(-1, 1, \frac{1}{2}\right)$ and $\nu_{e-} = 2$ | |
| B: | $\nu = \left(1, -1, -\frac{1}{2}\right)$ and $\nu_{e-} = 2$ | |
| C: | $\nu = (-2, 2, 1)$ and $\nu_{e-} = 4$ | |
| D: | $\nu = -(2, -2, -1)$ and $\nu_{e-} = 4$ | |

▲

## 1.2 Electrolyzer voltages

The so-called *chemical potential* $\mu_j$ of species $j$ in a mixture is given as molar Gibbs' energy $\tilde{G}_j^\circ$ of species $j$ at standard state plus a term $RT \cdot \ln a_j$ where $R$ is the gas constant, $T$ is absolute temperature (i.e., in K), and $a_j$ is the *activity*. Introducing $\mu_j \equiv \tilde{G}_j$, we have

$$\tilde{G}_j = \tilde{G}_j^\circ + RT \cdot \ln a_j. \tag{4}$$

For *ideal gas*,

$$a_j = \frac{p_j}{p^\circ} \tag{5}$$

where $p_j$ is the partial pressure of species $j$, while $p^\circ$ is a standard state *scaling* pressure (normally either 1 atm or 1 bar). In the liquid case, for an *ideal solution*

$$a_j = x_j \tag{6}$$

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where $x_j$ is the mole fraction $x_j = n_j/n$ of the liquid. For pure liquid $j$, $x_j = 1$.

The molar Gibbs energy of *reaction* $\Delta_r \tilde{G}$ (at arbitrary $T$, $p_j$) is given as

$$\Delta_r \tilde{G} = \sum_j \nu_j \tilde{G}_j, \tag{7}$$

while the *standard* molar Gibbs energy of reaction (i.e., at arbitrary $T$ and standard pressure $p°$) is denoted $\Delta_r \tilde{G}°$. The equilibrium voltage from the anode side (positive) to the cathode side (negative) is then

$$u_n = \frac{\Delta_r \tilde{G}}{F \nu_{e^-}} \tag{8}$$

where $F$ is *Faraday's number*.

**Problem 2.** Equilibrium voltage in Electrolyzer

The Nernst equilibrium voltage $u_n$ can be expressed in different ways.

| | **Problem 2:** Equilibrium voltage — which expression is **_incorrect_**? | Choice |
|---|---|---|
| A: | $u_n = \left( \Delta_r \tilde{G}° + RT \prod_j \ln a_j^{\nu_j} \right) / (F\nu_{e^-})$ | |
| B: | $u_n = \left( \Delta_r \tilde{G}° + RT \sum_j \ln a_j^{\nu_j} \right) / (F\nu_{e^-})$ | |
| C: | $u_n = \left( \Delta_r \tilde{G}° + RT \ln \left( \prod_j a_j^{\nu_j} \right) \right) / (F\nu_{e^-})$ | |
| D: | $u_n = \left( \Delta_r \tilde{G}°/\nu_{e^-} + RT \ln \left( \prod_j a_j^{\nu_j/\nu_{e^-}} \right) \right) / F$ | |

▲

Although various formulation are possible for $u_n$, it is numerically advantageous to compute $u_n$ by combining Eqs. 7 and 4 into equilibrium voltage $u_n$ (Nernst voltage) as

$$u_n = \underbrace{\frac{\sum_j \nu_j \tilde{G}_j°}{F\nu_{e^-}}}_{= \frac{\Delta_r \tilde{G}°}{F\nu_{e^-}} = u_\circ} + \underbrace{\frac{RT}{F\nu_{e^-}} \cdot \sum_j \nu_j \ln a_j}_{= u_p}, \tag{9}$$

where $u_\circ$ represents the equilibrium voltage at standard state (the actual temperature $T$, with standard state pressure $p° = 1\,\text{bar}$), while $u_p$ represents the pressure/activity dependent change in equilibrium voltage when $p \neq p°$. Here, molar Gibbs energy at standard state, $\tilde{G}_j°$, can to a good approximation be found from

$$\tilde{G}_j° = \Delta_f \tilde{G}_j° - \Delta_f \tilde{S}_j° (T - T°) + \tilde{c}_{p,j} (T - T°) - T \cdot \tilde{c}_{p,j} \ln \frac{T}{T°} \tag{10}$$

where for each species $j$, values for molar Gibbs energy of formation $\Delta_f \tilde{G}_j°$, molar entropy of formation $\Delta_f \tilde{S}_j°$, and molar heat capacity at constant pressure $\tilde{c}_{p,j}$ can be found in physical tables. For the overall equilibrium reaction $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$, this leads to the variation in $u_n$ with temperature as in Fig. 4.

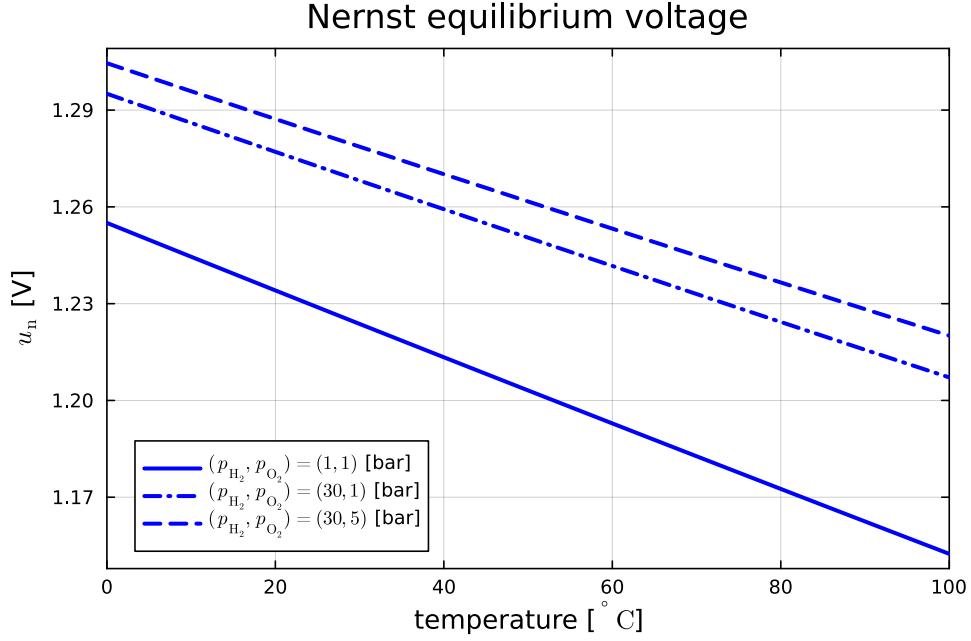**Problem 3.** Equilibrium voltage with pressure variation

Figure 4: Nernst voltage $u_n$ as a function of temperature for three combinations of $H_2$ and $O_2$ pressures.

In Fig. 4, the case $(p_{H_2}, p_{O_2}) = (1, 1)$ bar (solid line) represents $u_o$. From Fig. 4, the following assessments of $u_n$ can be given.

| | **Problem 3:** Equilibrium voltage — which statement is ***correct***? | Choice |
|---|---|---|
| A: | With increasing $H_2$ pressure and $O_2$ pressure, the equilibrium voltage decreases. | |
| B: | The pressure dependent change in equilibrium voltage $u_n$ is always a disadvantage. | |
| C: | With increasing $H_2$ pressure and $O_2$ pressure, the equilibrium voltage increases. | |
| D: | The pressure dependent change in equilibrium voltage $u_n$ is always an advantage. | |

▲

When current $i_c$ starts to flow through the cell, additional voltage drops occur, such as activation voltages ($u_a$) and membrane resistance voltage ($u_r$). These additional voltages are functions of temperature, but also of the current *density* $i''$, defined via Eq. 11,

$$i_c = A_c i'' \tag{11}$$

where $A_c$ is the membrane area of the cell. The resulting cell voltage $u_c$ is

$$u_c = u_n + u_a + u_r, \tag{12}$$

as in Fig. 5.

Note: with modern catalysts and thinner membranes, $u_c$ is typically down to 1.8 V or less $i'' = 2\,A/cm^2$.

**Problem 4.** Cell voltage

In the group project, the case $T = 60\,°C$ with pressures $(p_{H_2}, p_{O_2}) = (30, 1)$ bar was considered. Assume $\lambda = 18$ , and give estimates of $u_n$ and $u_c$ for these conditions at
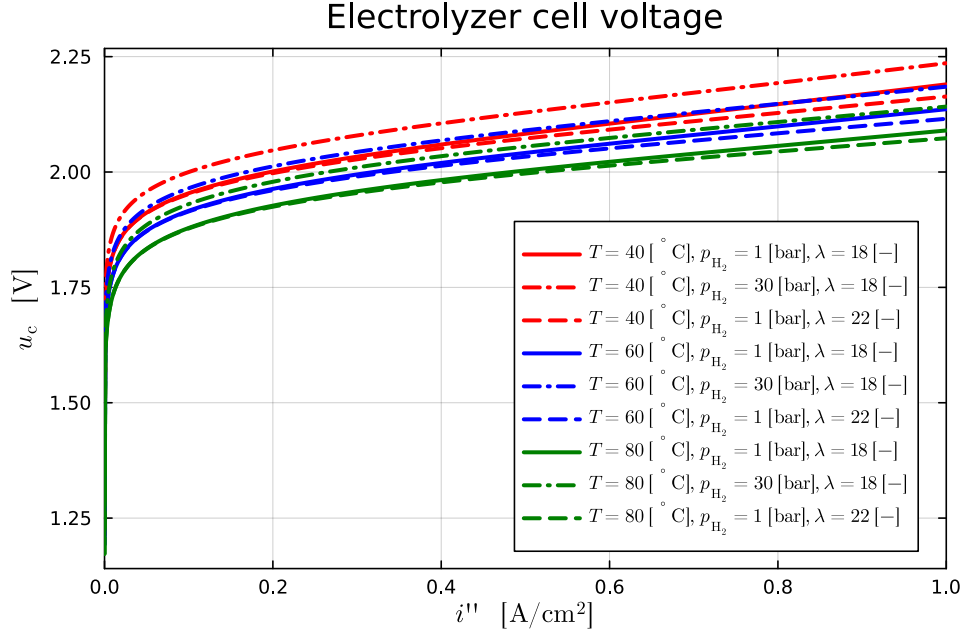
Figure 5: Electrolyzer cell voltage operating at $T = 40\,°C$ [red], $T = 60\,°C$ [blue], and $T = 80\,°C$ [green] at $p_{H_2} = 1\,\text{bar}, \lambda = 18$ [solid], $p_{H_2} = 30\,\text{bar}, \lambda = 18$ [dash-dot], and $p_{H_2} = 1\,\text{bar}, \lambda = 22$ [dash]; $p_{O_2} = 1\,\text{bar}$.

current density $i'' = 1\,\text{A/cm}^2$.

| | **Problem 4:** Equilibrium and cell voltages — which statement is ***correct***? | Choice |
|---|---|---|
| A: | $u_n \approx 1.20\,\text{V}$, $u_c \approx 2.15\,\text{V}$ | |
| B: | $u_n \approx 1.24\,\text{V}$, $u_c \approx 2.15\,\text{V}$ | |
| C: | $u_n \approx 1.24\,\text{V}$, $u_c \approx 2.00\,\text{V}$ | |
| D: | $u_n \approx 1.20\,\text{V}$, $u_c \approx 2.00\,\text{V}$ | |

▲

## 1.3 Electrolyzer stack design

Electric power consumption ("work" flow) in an electrolyzer stack is $\dot{W}_s = u_s i_s$ (unit: W) where $u_s$ (unit: V) is the stack voltage, while $i_s$ (unit: A) is the stack current. A stack consists of $N_c$ cells. PEM electrolyzer cells are normally organized electrically in series (bipolar cells), stack voltage $u_s$ is then

$$u_s = N_c u_c \tag{13}$$

where $u_c$ is the cell voltage, and stack current $i_s$ is

$$i_s = i_c \tag{14}$$

where $i_c$ is the current through a cell.

Generation of species $j$ can be expressed as

$$\dot{n}_j^g = \nu_j \dot{n}_g \tag{15}$$

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where the *generation rate* $\dot{n}_{\mathrm{g}}$ is

$$\dot{n}_{\mathrm{g}} = \frac{N_{\mathrm{c}} A_{\mathrm{c}}}{\nu_{\mathrm{e}^-} F} i''. \tag{16}$$

The corresponding mass generation rate is

$$\dot{m}_j^{\mathrm{g}} = M_j \dot{n}_j^{\mathrm{g}} = M_j \frac{\nu_j N_{\mathrm{c}} A_{\mathrm{c}}}{\nu_{\mathrm{e}^-} F} i'', \tag{17}$$

where a negative value for $\dot{n}_j^{\mathrm{g}}$ and $\dot{m}_j^{\mathrm{g}}$ indicates *consumption*.

In the design of a stack, assume that maximally allowed current density is $i''_{\max}$, which leads to a corresponding maximal cell voltage $u_{\mathrm{c}}(i''_{\max})$. With $N_{\mathrm{c}}$ cells in the stack, the maximal electric power $\dot{W}_{\mathrm{s}}^{\max}$ added to the stack is

$$\dot{W}_{\mathrm{s}}^{\max} = u_{\mathrm{s}}^{\max} i_{\mathrm{s}}^{\max} = N_{\mathrm{c}} u_{\mathrm{c}}(i''_{\max}) i_{\mathrm{c}}^{\max} = N_{\mathrm{c}} A_{\mathrm{c}} i''_{\max} \cdot u_{\mathrm{c}}(i''_{\max}). \tag{18}$$

By combining Eqs. 17 and 18, the corresponding maximal hydrogen production is

$$\dot{m}_{\mathrm{H}_2}^{\max} = \frac{\nu_{\mathrm{H}_2} M_{\mathrm{H}_2}}{\nu_{\mathrm{e}^-} F} N_{\mathrm{c}} A_{\mathrm{c}} i''_{\max}. \tag{19}$$

Solving Eq. 19 for $N_{\mathrm{c}} A_{\mathrm{c}} i''_{\max}$ and inserting the resulting expression into Eq. 18, it follows that with a specified hydrogen production rate, the required electric power delivery to the stack is

$$\dot{W}_{\mathrm{s}}^{\max} = \frac{\nu_{\mathrm{e}^-} F \cdot u_{\mathrm{c}}(i''_{\max})}{\nu_{\mathrm{H}_2} M_{\mathrm{H}_2}} \dot{m}_{\mathrm{H}_2}^{\max}. \tag{20}$$

From Eq. 18, and with $\dot{W}_{\mathrm{s}}^{\max}$ as in Eq. 20, we can find the total membrane area $A_{\mathrm{s}}$ of the stack as

$$A_{\mathrm{s}} = N_{\mathrm{c}} A_{\mathrm{c}} = \frac{\dot{W}_{\mathrm{s}}^{\max}}{i''_{\max} u_{\mathrm{c}}(i''_{\max})}. \tag{21}$$

**Problem 5.** Stack design I

In the project group, the following data were used

$$i''_{\max} = 2\,\mathrm{A/cm}^2$$
$$M_{\mathrm{H}_2} = 2\,\mathrm{g/mol} = 2 \cdot 10^{-3}\,\mathrm{kg/mol}$$
$$F = 9.649 \cdot 10^4\,\mathrm{C/mol}$$

For simplicity, set $u_{\mathrm{c}}(i''_{\max}) = 2.5\,\mathrm{V}$ (note: Fig. 5 only displays $u_{\mathrm{c}}$ for $i'' \in [0,1]$). With required production $\dot{m}_{\mathrm{H}_2}^{\max} = 24\,\mathrm{kg/h} = \frac{24}{3600}\,\mathrm{kg/s}$, find the numeric value of the stack membrane area $A_{\mathrm{s}} = N_{\mathrm{c}} A_{\mathrm{c}}$.

| | **Problem 5:** With the given data, the stack membrane area $A_{\mathrm{s}}$ is — which value is **correct?** | Choice |
|---|---|---|
| A: | $A_{\mathrm{s}} \approx 160\,\mathrm{m}^2$ | |
| B: | $A_{\mathrm{s}} \approx 1.6 \cdot 10^6\,\mathrm{m}^2$ | |
| C: | $A_{\mathrm{s}} \approx 3.2 \cdot 10^5\,\mathrm{m}^2$ | |
| D: | $A_{\mathrm{s}} \approx 32\,\mathrm{m}^2$ | |

▲

With a required stack membrane area $A_{\mathrm{s}}$, choice of cell membrane area $A_{\mathrm{c}}$ provides the required number of cells $N_{\mathrm{c}}$. In the group project, the membrane area was set to $A_{\mathrm{c}} = 160\,\mathrm{cm}^2$, which lead to $N_{\mathrm{c}} \approx 2000$.

In industrial design, typically $A_c$ is in the range of 400–500 cm$^2$. Furthermore, normally $N_c$ is rarely larger than $N_c = 200$. If the realistic values for $N_c$ and $A_c$ lead to a stack membrane area $A_s = N_c A_c$ that is smaller than what is required by Eq. 21, a possible solution is to connect several stacks in parallel.

**Problem 6.** Stack design II

With $N_c = 200$, the stack voltage is $u_s = N_c u_c$ or with $u_c = u_c (i''_{\max}) = 2.5\,\mathrm{V}$, around 500 V. Assuming $A_c = 400\,\mathrm{cm}^2$, the total area for the stack is $N_s = N_c A_c = 8 \cdot 10^4\,\mathrm{cm}^2$, which is smaller than the required number $N_s$ found in Problem 5.

To achieve the required production of $\dot{m}_{\mathrm{H_2}}^{\max}$, we therefore need to operate with more than one stack in parallel. It is also of interest to consider the maximal total current into the stack system.

| | **Problem 6:** The minimal number of stacks ($A_c = 400\,\mathrm{cm}^2$, $N_c = 200$), and the resulting total current for the system are — which answer is **correct?** | Choice |
|---|---|---|
| A: | We need 3 stacks, and the total current is $i = 800\,\mathrm{A}$. | |
| B: | We need 3 stacks, and the total current is $i = 8\,\mathrm{kA}$. | |
| C: | We need 4 stacks, and the total current is $i = 320\,\mathrm{A}$. | |
| D: | We need 4 stacks, and the total current is $i = 3.2\,\mathrm{kA}$. | |

▲

## 1.4 Electrolyzer dynamics

Figure 6 is taken from the group project, and depicts the anode water/O$_2$ gas separator system, see also Fig. 2.

The generation rates $\dot{n}_j^{\mathrm{g}}$ are given by Eqs. 15 and 16. Electro-osmotic water drag through the membrane of *a single cell* is given by

$$\dot{n}_{\mathrm{H_2O}}^{\mathrm{m,d}} = \eta_{\mathrm{d}} \cdot \frac{A_c i''}{F}; \tag{22}$$

assume that $\eta_{\mathrm{d}}$ is known. Assume that $\dot{n}_{\mathrm{H_2O}}^{\mathrm{i}}$ is given (in the project: a P-controller was used) and $\dot{n}_{\mathrm{H_2O}}^{\mathrm{c,r}}$ is given (in the project: a P-controller was used). With water saturation pressure $p_{\mathrm{H_2O}}^{\mathrm{sat}}$ a known function of temperature $T$, the volumetric flow out of the top valve is given by

$$\dot{V}_{\mathrm{a}}^{\mathrm{e}} = \dot{V}_{\mathrm{a}}^{\varsigma}\frac{p_{\mathrm{a}} - p_{\mathrm{a}}^{\mathrm{e}}}{p^{\circ}} \tag{23}$$

where the total anode pressure $p_{\mathrm{a}}$ is

$$p_{\mathrm{a}} = p_{\mathrm{O_2}}^{\mathrm{a}} + p_{\mathrm{H_2O}}^{\mathrm{sat}}. \tag{24}$$

Flows of oxygen and water vapor out with $\dot{V}_{\mathrm{a}}^{\mathrm{e}}$ are given by the flow-version of the ideal gas law

$$pV = nRT, \tag{25}$$

i.e., by

$$p_j \dot{V} = \dot{n}_j RT. \tag{26}$$

In the group project, water vapor leaving the anode tank via the gas valve (Eqs. 26, 23), $\dot{n}_{\mathrm{H_2O,gas}}^{\mathrm{a,e}}$, was neglected.
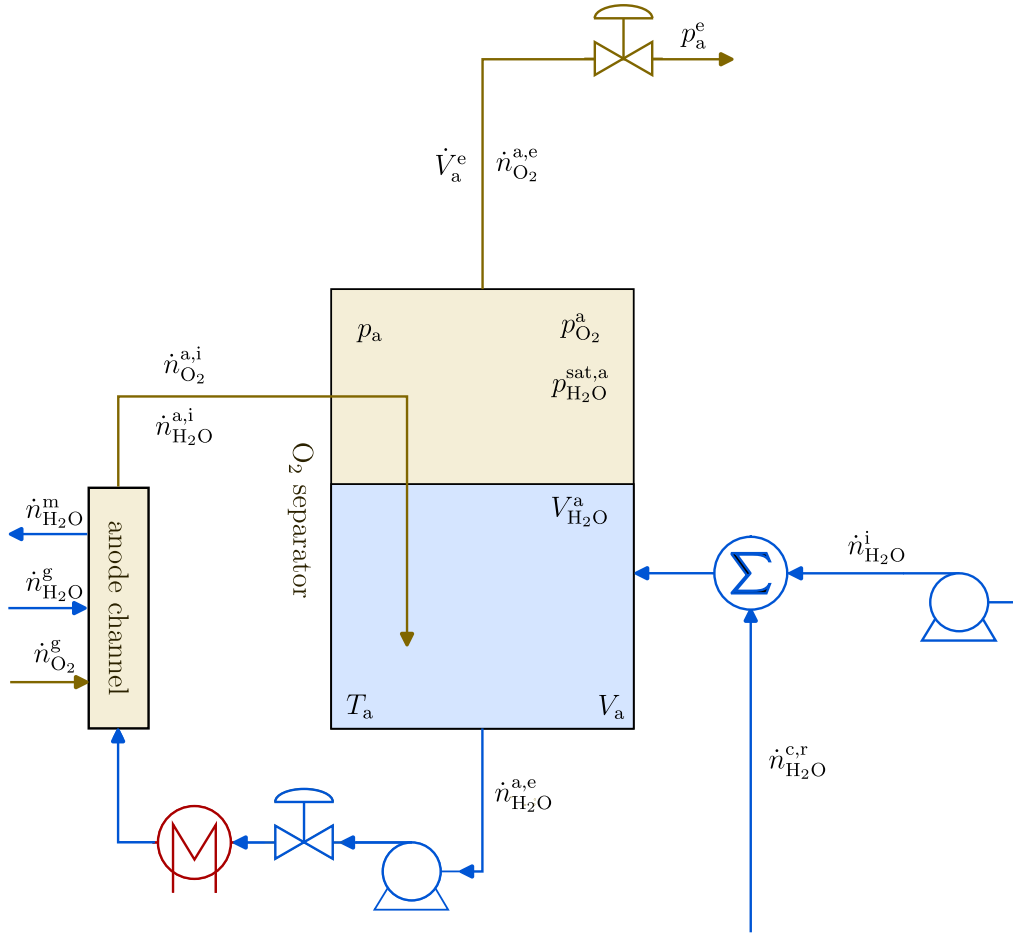
Figure 6: Anode oxygen-water separator subsystem. Note that generation $\dot{n}_{H_2O}^{g}$ is negative (consumption), which means that the actual flow is against the arrow direction.

**Problem 7.** Anode tank water balance.

Using the symbols in Fig. 6 and the given expressions, formulate the mass balance for water in the separator tank, and find a differential equation for the water volume in the anode, $V_{H_2O}^a$, when assuming $\dot{n}_{H_2O,gas}^{a,e} = 0$.

| | **Problem 7:** The water volume in the anode, $V_{H_2O}^a$, is given by the following differential equation — which answer is **correct**? | Choice |
|---|---|---|
| A: | $\frac{dV_{H_2O}^a}{dt} = \left( \dot{n}_{H_2O}^i - \dot{n}_{H_2O}^{c,r} + N_c \left( \eta_d - \frac{\nu_{H_2O}}{\nu_{e^-}} \right) \cdot \frac{A_c i''}{F} \right) / \frac{\rho_{H_2O}}{M_{H_2O}}$ | |
| B: | $\frac{dV_{H_2O}^a}{dt} = \left( \dot{n}_{H_2O}^i - \dot{n}_{H_2O}^{c,r} - N_c \left( \eta_d - \frac{\nu_{H_2O}}{\nu_{e^-}} \right) \cdot \frac{A_c i''}{F} \right) / \frac{\rho_{H_2O}}{M_{H_2O}}$ | |
| C: | $\frac{dV_{H_2O}^a}{dt} = \left( \dot{n}_{H_2O}^i + \dot{n}_{H_2O}^{c,r} - N_c \left( \eta_d - \frac{\nu_{H_2O}}{\nu_{e^-}} \right) \cdot \frac{A_c i''}{F} \right) / \frac{\rho_{H_2O}}{M_{H_2O}}$ | |
| D: | $\frac{dV_{H_2O}^a}{dt} = \left( \dot{n}_{H_2O}^i + \dot{n}_{H_2O}^{c,r} + N_c \left( \eta_d - \frac{\nu_{H_2O}}{\nu_{e^-}} \right) \cdot \frac{A_c i''}{F} \right) / \frac{\rho_{H_2O}}{M_{H_2O}}$ | |

▲

**Problem 8.** Anode tank oxygen balance.

Using the symbols in Fig. 6 and additional expressions, formulate the mass balance for oxygen in the separator tank and find a model for the oxygen partial pressure $p_{O_2}^a$ in the anode tank.

| | **Problem 8:** The oxygen pressure in the anode separator tank, $p_{O_2}^a$, is given by the following differential equation — which answer is **correct**? [Hint: $\frac{dV_{H_2O}^a}{dt}$ is given in Problem 7]. | Choice |
|---|---|---|
| A: | $\frac{dp_{O_2}^a}{dt} = \left( p_{O_2}^a \frac{dV_{H_2O}^a}{dt} + N_c \frac{\nu_{O_2}}{\nu_{e^-}} \frac{A_c}{F} i'' - \frac{p_{O_2}^a}{RT} \dot{V}_a^\varsigma \frac{p_a^a + p_{H_2O}^{sat} - p_a^e}{p^\circ} \right) / \left( V_a - V_{H_2O}^a \right)$ | |
| B: | $\frac{dp_{O_2}^a}{dt} = \left( p_{O_2}^a \frac{dV_{H_2O}^a}{dt} + N_c \frac{\nu_{O_2}}{\nu_{e^-}} \frac{A_c}{F} i'' - \frac{p_{O_2}^a}{RT} \dot{V}_a^\varsigma \frac{p_a^a + p_{H_2O}^{sat} - p_a^e}{p^\circ} \right) / V_a$ | |
| C: | $\frac{dp_{O_2}^a}{dt} = \left( -p_{O_2}^a \frac{dV_{H_2O}^a}{dt} + N_c \frac{\nu_{O_2}}{\nu_{e^-}} \frac{A_c}{F} i'' - \frac{p_{O_2}^a}{RT} \dot{V}_a^\varsigma \frac{p_a^a + p_{H_2O}^{sat} - p_a^e}{p^\circ} \right) / \left( V_a - V_{H_2O}^a \right)$ | |
| D: | $\frac{dp_{O_2}^a}{dt} = \left( -p_{O_2}^a \frac{dV_{H_2O}^a}{dt} + N_c \frac{\nu_{O_2}}{\nu_{e^-}} \frac{A_c}{F} i'' - \frac{p_{O_2}^a}{RT} \dot{V}_a^\varsigma \frac{p_a^a + p_{H_2O}^{sat} - p_a^e}{p^\circ} \right) / V_a$ | |

▲

Let $\dot{n}_{H_2O,gas}^{a,e}$ be the rate at which water is lost to the atmosphere through the anode effluent gas valve. In the group project, this loss of water was neglected.

The fractional water loss $x_{H_2O}^a$ loss can be defined as

$$x_{H_2O}^a \triangleq \frac{\dot{n}_{H_2O,gas}^{a,e}}{\dot{n}_{H_2O,gas}^{a,e} + \dot{n}_{O_2}^{a,e}}, \tag{27}$$

where the flow version of the ideal gas law is as in Eq. 26.

**Problem 9.** Anode tank pressure vs. water loss.

It is of interest to find whether, and if so, how the anode pressure $p_a$ influences the fraction $x_{H_2O}^a$ in Eq. 27.

| | **Problem 9:** The mole fraction of water transported through the anode gas exit valve is — which answer is **correct**? | Choice |
|---|---|---|
| A: | $x_{H_2O}^a = \frac{p_{H_2O}^{sat}}{p_a - p_{H_2O}^{sat}}$ | |
| B: | $x_{H_2O}^a = \frac{p_{H_2O}^{sat}}{p_a^e} = $ constant | |
| C: | $x_{H_2O}^a = \frac{p_{H_2O}^{sat}}{p_a - p_a^e}$ | |
| D: | $x_{H_2O}^a = \frac{p_{H_2O}^{sat}}{p_a}$ | |

**Problem 10.** Anode tank time constant.

The transfer functions from current density $i''$ to anode tank oxygen pressure $p_{O_2}^a$ and water volume $\dot{V}_{H_2O}^a$ were given in the group project solution report as

$$\frac{p_{O_2}^a}{i''} \propto \frac{(1 + 2.26s)\,(1 + 4.7s)}{(1 + 0.04s)\,(1 + 2.3s)\,(1 + 4.6s)} \tag{28}$$

$$\frac{V_{H_2O}^a}{i''} \propto \frac{1 + 23s}{(1 + 2.3s)\,(1 + 4.6s)} \tag{29}$$

with time given in minutes, and symbol "$\propto$" means "is proportional to" [i.e., $\frac{V_{H_2O}^a}{i''}$ is proportional to $\frac{1+23s}{(1+2.3s)(1+4.6s)}$, etc.].

|  | **Problem 10:** The time constants of the water/$O_2$ separator tank are — which answer is **correct?** | Choice |
|---|---|---|
| A: | $T_1 = 2.26\,\mathrm{min}$, $T_2 = 4.7\,\mathrm{min}$, $T_3 = 23\,\mathrm{min}$ | |
| B: | $T_1 = 2.26\,\mathrm{min}$, $T_2 = 4.7\,\mathrm{min}$, $T_3 = 23\,\mathrm{min}$, $T_4 = 2.4\,\mathrm{s}$, $T_5 = 2.3\,\mathrm{min}$, $T_6 = 4.6\,\mathrm{min}$ | |
| C: | $T_1 = 0.04\,\mathrm{min}$, $T_2 = 4.6\,\mathrm{min}$ | |
| D: | $T_1 = 2.4\,\mathrm{s}$, $T_2 = 2.3\,\mathrm{min}$, $T_3 = 4.6\,\mathrm{min}$ | |

## 1.5 Stack energy balance

In the group project, it was assumed that the temperature was constant ($T = 60\,°\mathrm{C}$) and the same everywhere in the system. In reality, the temperature will vary, depending on how the system is operated.

Here, we will assume that the *stack* has homogeneous, possibly time varying temperature $T_\mathrm{s}$, but that the rest of the system, including separator tanks, has constant temperature $T$. To find how $T_\mathrm{s}$ varies, we consider the energy balance for the stack.

The thermal energy balance can be written as

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \dot{H}_\mathrm{i} - \dot{H}_\mathrm{e} + \dot{W} + \dot{Q}, \tag{30}$$

where internal energy $U$ is related to enthalpy $H$ and pressure-volume $pV$ as

$$U = H - pV. \tag{31}$$

Assuming an *ideal solution*, we have

$$H \approx \sum_j H_\mathrm{j} = \sum_j n_j \tilde{H}_j = \sum_j m_j \hat{H}_j \tag{32}$$

$$\dot{H} \approx \sum_j \dot{H}_j = \sum_j \dot{n}_j \tilde{H}_j = \sum_j \dot{m}_j \hat{H}_j; \tag{33}$$

in the expression for $H$, a term $n_j \tilde{H}_j$ may be replaced by $m_j \hat{H}_j$ , and in the expression for $\dot{H}$, a term $\dot{n}_j \tilde{H}_j$ may be replaced by $\dot{m}_j \hat{H}_j$ if this is more convenient. The stack system

consists of metal with mass $m_s$ and heat capacity $\hat{c}_{p,s}$, as well as fluids (water, hydrogen, oxygen) with amounts $n_j$ and heat capacity $\tilde{c}_{p,j}$. For simplicity, assume that

$$\tilde{H}_j \approx \tilde{H}_j^\circ + \tilde{c}_{p,j}\left(T - T^\circ\right) \tag{34}$$

$$\hat{H}_j \approx \hat{H}_j^\circ + \hat{c}_{p,j}\left(T - T^\circ\right). \tag{35}$$

The main work rate $\dot{W}$ added to the system consists of electric power; possible friction loss will be neglected here:

$$\dot{W} = u_s i_s = N_c u_c\left(i'', T\right) i_c \tag{36}$$

where $i_c$ and $i''$ are related as in Eq. 11, and $u_c\left(i'', T\right)$ is the applied cell voltage $u_c$, Eq. 12. Added heat consists of convective heat $\dot{Q}_v$ and heat by radiation $\dot{Q}_r$,

$$\dot{Q} = \dot{Q}_v + \dot{Q}_r, \tag{37}$$

where

$$\dot{Q}_v = A_s \mathcal{U}_s\left(T_a - T_s\right) \tag{38}$$

$$\dot{Q}_r = A_s \varepsilon_s \sigma\left(T_a^4 - T_s^4\right); \tag{39}$$

$A_s$ is the surface area of the stack, $\mathcal{U}_s$ is the stack overall heat transfer coefficient, $T_a$ is the ambient temperature, $T_s$ is the stack temperature, $\varepsilon_s$ is the surface emmisivity, and $\sigma$ is the Stefan-Boltzmann constant.

**Problem 11.** Stack energy balance — net enthalpy flow

In the energy balance, it is of interest to find an expression for the net enthalpy influent $\Delta\dot{H}$,

$$\Delta\dot{H} \triangleq \dot{H}_i - \dot{H}_e. \tag{40}$$

As part of $\Delta\dot{H}$, the enthalpy of reaction $\Delta_r\tilde{H}$ will appear,

$$\Delta_r\tilde{H} \triangleq \sum_j \nu_j \tilde{H}_j. \tag{41}$$

Show that the net enthalpy flow $\Delta\dot{H}$ through the stack can be expressed as

| | **Problem 11:** Net enthalpy flow $\Delta\dot{H}$ through the stack can be expressed as — which expression is **correct**? | Choice |
|---|---|---|
| A: | $\Delta\dot{H} = -N_c \frac{\Delta_r\tilde{H}}{F\nu_{e^-}} A_c i''$ | |
| B: | $\Delta\dot{H} = \dot{n}_{H_2O}^{a,e} \tilde{c}_{p,H_2O}\left(T - T_s\right) - N_c \frac{\Delta_r\tilde{H}}{F\nu_{e^-}} A_c i''$ | |
| C: | $\Delta\dot{H} = \dot{n}_{H_2O}^{a,e} \tilde{c}_{p,H_2O}\left(T - T_s\right) + N_c \frac{\Delta_r\tilde{H}}{F\nu_{e^-}} A_c i''$ | |
| D: | $\Delta\dot{H} = -\dot{n}_{H_2O}^{a,e} \tilde{c}_{p,H_2O}\left(T - T_s\right) - N_c \frac{\Delta_r\tilde{H}}{F\nu_{e^-}} A_c i''$ | |

▲

Similarly to the Nernst equilibrium voltage $u_n$ which can be expressed as in Eq. 8, $u_n = \frac{\Delta_r\tilde{G}}{F\nu_{e^-}}$, we can define the so-called *thermoneutral* voltage $u_{th}$ as

$$u_{th} \triangleq \frac{\Delta_r\tilde{H}}{F\nu_{e^-}}. \tag{42}$$

Observe that

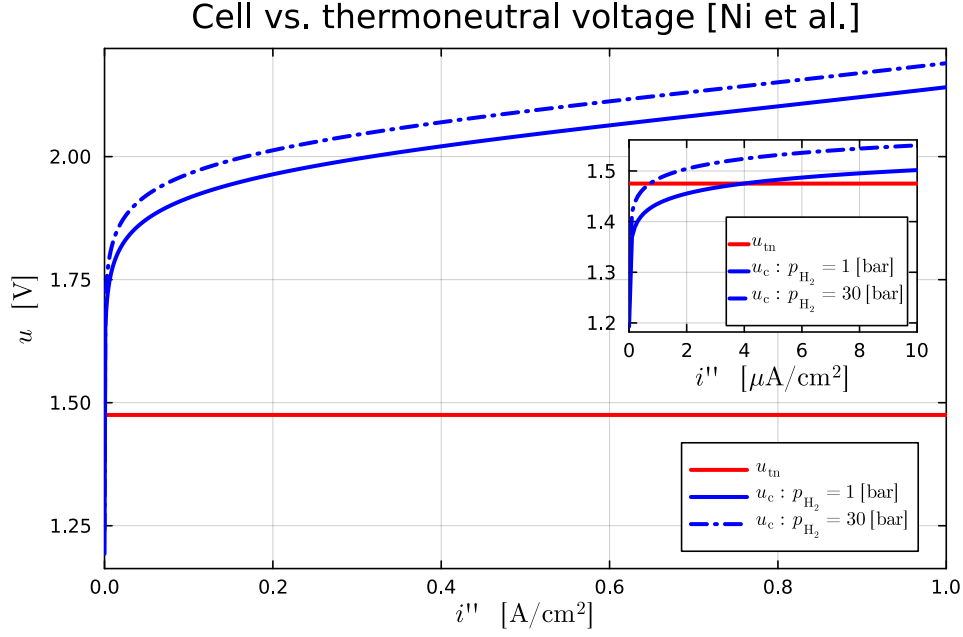$$\Delta_r\tilde{H} = \Delta_r\tilde{G} + T\Delta_r\tilde{S} > \Delta_r\tilde{G} \Rightarrow u_{th} > u_n. \tag{43}$$

Figure 7: Comparing temperature variation in thermoneutral voltage $u_{\text{tn}}$ and cell voltage $u_{\text{c}}$.

**Problem 12.** Stack energy balance — ODE

Assume that the internal energy $U$ is approximately equal to the internal energy of metal, and assume that $pV = $ constant. Show that the differential equation for the temperature can be written as

| | **Problem 12:** Ordinary differential equation for stack temperature $T_{\text{s}}$ — which expression is **correct**? | Choice |
|---|---|---|
| A: | $\dfrac{\mathrm{d}T_{\text{s}}}{\mathrm{d}t} = \dfrac{\dot{n}_{\text{H}_2\text{O}}^{\text{a,e}}\tilde{c}_{\text{p,H}_2\text{O}}(T-T_{\text{s}})+N_{\text{c}}A_{\text{c}}i''(u_{\text{th}}-u_{\text{c}})+A_{\text{s}}\left(\mathcal{U}_{\text{s}}(T_{\text{a}}-T_{\text{s}})+\varepsilon_{\text{s}}\sigma\left(T_{\text{a}}^4-T_{\text{s}}^4\right)\right)}{m_{\text{s}}}$ | |
| B: | $\dfrac{\mathrm{d}T_{\text{s}}}{\mathrm{d}t} = \dfrac{\dot{n}_{\text{H}_2\text{O}}^{\text{a,e}}\tilde{c}_{\text{p,H}_2\text{O}}(T-T_{\text{s}})+N_{\text{c}}A_{\text{c}}i''(u_{\text{c}}-u_{\text{th}})+A_{\text{s}}\left(\mathcal{U}_{\text{s}}(T_{\text{a}}-T_{\text{s}})+\varepsilon_{\text{s}}\sigma\left(T_{\text{a}}^4-T_{\text{s}}^4\right)\right)}{m_{\text{s}}\hat{c}_{\text{p,s}}}$ | |
| C: | $\dfrac{\mathrm{d}T_{\text{s}}}{\mathrm{d}t} = \dfrac{\dot{n}_{\text{H}_2\text{O}}^{\text{a,e}}\tilde{c}_{\text{p,H}_2\text{O}}(T-T_{\text{s}})+N_{\text{c}}A_{\text{c}}i''(u_{\text{c}}-u_{\text{th}})+A_{\text{s}}\left(\mathcal{U}_{\text{s}}(T_{\text{a}}-T_{\text{s}})+\varepsilon_{\text{s}}\sigma\left(T_{\text{a}}^4-T_{\text{s}}^4\right)\right)}{m_{\text{s}}}$ | |
| D: | $\dfrac{\mathrm{d}T_{\text{s}}}{\mathrm{d}t} = \dfrac{\dot{n}_{\text{H}_2\text{O}}^{\text{a,e}}\tilde{c}_{\text{p,H}_2\text{O}}(T-T_{\text{s}})-N_{\text{c}}A_{\text{c}}i''(u_{\text{c}}-u_{\text{th}})+A_{\text{s}}\left(\mathcal{U}_{\text{s}}(T_{\text{a}}-T_{\text{s}})+\varepsilon_{\text{s}}\sigma\left(T_{\text{a}}^4-T_{\text{s}}^4\right)\right)}{m_{\text{s}}\hat{c}_{\text{p,s}}}$ | |

▲

The cell voltage $u_{\text{c}}$ depends on current density $i''$ and temperature $T_{\text{s}}$, while the thermoneutral voltage $u_{\text{th}}$ only depends on temperature $T_{\text{s}}$. Figure 7 illustrates $u_{\text{c}}$ and $u_{\text{th}}$ as a function of current density $i''$.

**Problem 13.** The role of thermoneutral voltage

The value of the thermoneutral voltage $u_{\text{th}}$ may or may not influence the stack temperature $T_{\text{s}}$. Which of the following statements is correct?
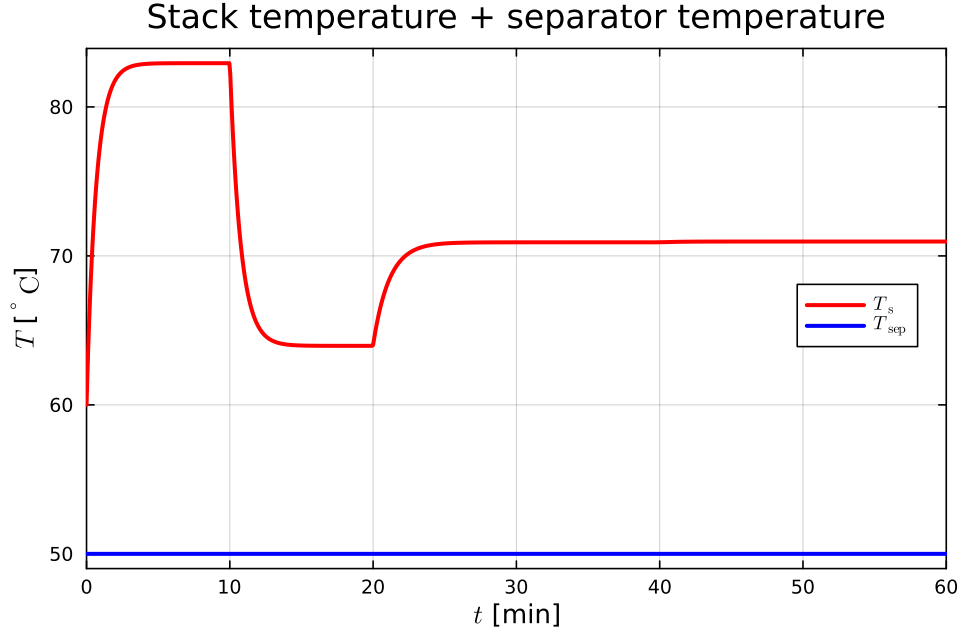
Figure 8: Stack temperature $T_s$ and assumed perfectly constant separator volume temperatures $T_{sep} = T$.

| | Problem 13: How does the thermoneutral voltage affect the stack temperature — which statement is correct? | Choice |
|---|---|---|
| A: | The thermoneutral voltage $u_{th}$ has no effect on the stack temperature. | |
| B: | The thermoneutral voltage $u_{th}$ is a fictitious voltage that is only used in efficiency computations. | |
| C: | If the cell voltage $u_c$ is smaller than the thermoneutral voltage $u_{th}$, $u_c < u_{th}$, this will heat the stack. | |
| D: | If the cell voltage $u_c$ is larger than the thermoneutral voltage $u_{th}$, $u_c > u_{th}$, this will heat the stack. | |

▲

Using the group project case as an example, but keeping the water in the anode tank at $T = T_{sep} = 50\,°C$ while *reducing* the current density $i''$ at $t = 10\,min$, *reducing* the anode channel circulation $\dot{n}_{H_2O}^{a,e}$ at $t = 20\,min$, and *increasing* the ambient temperature $T_a$ at $t = 40\,min$ the temperature, the stack temperature $T_s$ varies as in Fig. 8

In Fig. 8, the initial increase in $T_s$ (at $t = 0$) is the result of starting the simulation away from steady state.

**Problem 14.** Thermal time constant

Give an estimate of the thermal time constant of the system based on Fig. 8.

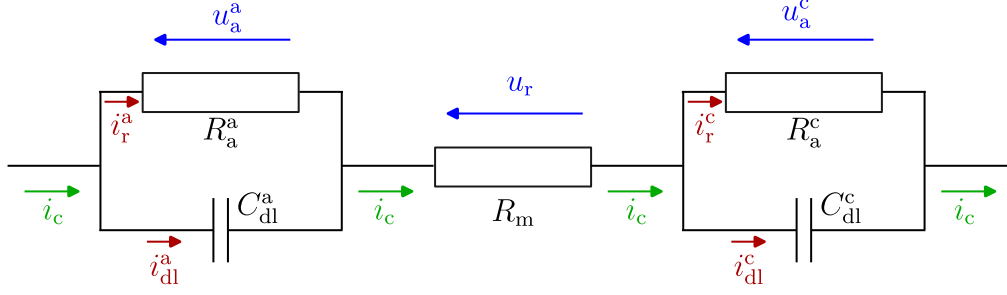| | Problem 14: The thermal time constant of the stack is — which statement is correct? | Choice |
|---|---|---|
| A: | It is not possible to assess the thermal time constant from Fig. 8. | |
| B: | The thermal time constant is approximately $2\,min$ | |
| C: | The thermal time constant is approximately $10\,min$ | |
| D: | The thermal time constant is approximately $25\,min$ | |

▲

Figure 9: Equivalent linear electric model for kinetics of membrane.

## 1.6 Stack electrodynamics

In the group project, possible dynamics in the electric part of the membrane has been neglected. In reality, on the electrode interface between the catalyst and the membrane, there is a so-called *double layer* capacitor with capacitance $C_{\mathrm{dl}}$, one for the anode ($C_{\mathrm{dl}}^{\mathrm{a}}$) and one for the cathode ($C_{\mathrm{dl}}^{\mathrm{c}}$). For simplicity, assume that the capacitance is the same for both electrodes, i.e., $C_{\mathrm{dl}}^{\mathrm{a}} = C_{\mathrm{dl}}^{\mathrm{c}} = C_{\mathrm{dl}}$. It is common to express $C_{\mathrm{dl}}$ as

$$C_{\mathrm{dl}} = A_{\mathrm{c}} C_{\mathrm{dl}}'', \tag{44}$$

where $C_{\mathrm{dl}}''$ is the double-layer capacitance per cell membrane area $A_{\mathrm{c}}$.

The capacitors are electrically in parallel with the activation voltage drops $u_{\mathrm{a}}$, with $u_{\mathrm{a}}^{\mathrm{a}}$ for the anode (OER, oxygen reaction), and $u_{\mathrm{a}}^{\mathrm{c}}$ for the cathode (HER, hydrogen reaction). The activation voltages $u_{\mathrm{a}}$ are functions of current density $i''$, and therefore of current $i_{\mathrm{c}}$.

From an electrical engineering point of view, this means that the relationship $u_{\mathrm{a}} = u_{\mathrm{a}}(i'')$ can be considered a non-linear resistor voltage drop, in other words: by linearizing this voltage drop around the operating point, we get $u_{\mathrm{a}}^{\delta} \approx R_{\mathrm{a}} i_{\mathrm{r}}^{\delta}$ where $u_{\mathrm{a}}^{\delta}$ and $i_{\mathrm{r}}^{\delta}$ are deviations from their respective operating points. Thus, one parallel RC circuit at both of the electrodes ($C_{\mathrm{dl}}^{\mathrm{a}} = C_{\mathrm{dl}}$, $R_{\mathrm{a}}^{\mathrm{a}}$, and $C_{\mathrm{dl}}^{\mathrm{c}} = C_{\mathrm{dl}}$, $R_{\mathrm{a}}^{\mathrm{c}}$), separated by the membrane resistor $R_{\mathrm{m}}$, Fig. 9.

Figure 9 shows the relevant currents $i_{\mathrm{c}}$ (green color), $i_{\mathrm{r}}^{\mathrm{a}}$, $i_{\mathrm{dl}}^{\mathrm{a}}$, $i_{\mathrm{r}}^{\mathrm{c}}$, and $i_{\mathrm{dl}}^{\mathrm{c}}$ (red color), as well as relevant voltages $u_{\mathrm{a}}^{\mathrm{a}}$, $u_{\mathrm{r}}$, and $u_{\mathrm{a}}^{\mathrm{c}}$ (blue color). Because the depicted circuit in Fig. 9 is linear, the order of the blocks is irrelevant, and we will neglect the membrane resistor $R_{\mathrm{m}}$ in the sequel; we will set the *total* activation voltage $u_{\mathrm{a}}$ equal to the *sum* of activation voltage losses on the anode ($u_{\mathrm{a}}^{\mathrm{a}}$) and the cathode ($u_{\mathrm{a}}^{\mathrm{c}}$).

Because the course syllabus for course FM1015 Modelling of Dynamic Systems does not include modeling of electric circuits, the model for the activation voltages is given below for convenience:

$$C_{\mathrm{dl}}^{\mathrm{a}} \frac{\mathrm{d}u_{\mathrm{a}}^{\mathrm{a}}}{\mathrm{d}t} = i_{\mathrm{dl}}^{\mathrm{a}} \tag{45}$$

$$u_{\mathrm{a}}^{\mathrm{a}} = R_{\mathrm{a}}^{\mathrm{a}} i_{\mathrm{r}}^{\mathrm{a}} \tag{46}$$

$$i_{\mathrm{c}} = i_{\mathrm{r}}^{\mathrm{a}} + i_{\mathrm{dl}}^{\mathrm{a}} \tag{47}$$

$$C_{\mathrm{dl}}^{\mathrm{c}} \frac{\mathrm{d}u_{\mathrm{a}}^{\mathrm{c}}}{\mathrm{d}t} = i_{\mathrm{dl}}^{\mathrm{c}} \tag{48}$$

$$u_{\mathrm{a}}^{\mathrm{c}} = R_{\mathrm{a}}^{\mathrm{c}} i_{\mathrm{r}}^{\mathrm{a}} \tag{49}$$

$$i_{\mathrm{c}} = i_{\mathrm{r}}^{\mathrm{c}} + i_{\mathrm{dl}}^{\mathrm{c}} \tag{50}$$

$$u_{\mathrm{a}} = u_{\mathrm{a}}^{\mathrm{a}} + u_{\mathrm{a}}^{\mathrm{c}}. \tag{51}$$
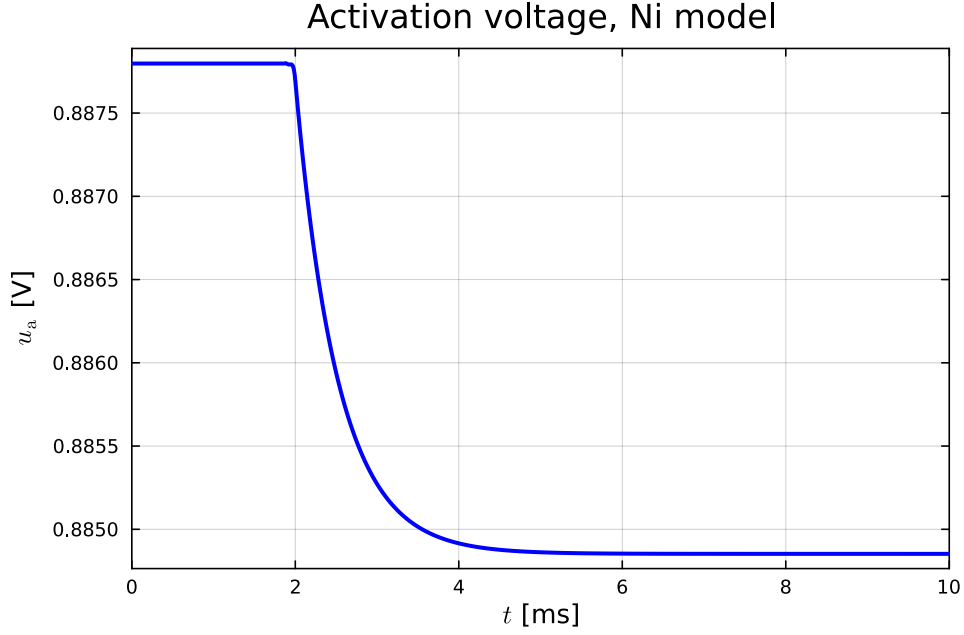
Figure 10: Activation voltage $u_\mathrm{a}$ after a step change in current density $i''$.

**Problem 15.** Electrodynamics — transfer function

It is of interest to find the *transfer function $h(s)$* from external current $i_\mathrm{c}$ to total activation voltage loss $u_\mathrm{a}$, i.e.,

$$u_\mathrm{a}(s) = h(s) \cdot i_\mathrm{c}(s). \tag{52}$$

| | **Problem 15:** Which expression for the transfer function from $i_\mathrm{c}(s)$ to $u_\mathrm{a}(s)$, denoted $h(s)$, is ***correct***? | Choice |
|---|---|---|
| A: | $h(s) = \frac{R_\mathrm{a}^\mathrm{a}}{1+R_\mathrm{a}^\mathrm{a}C_\mathrm{dl}^\mathrm{a}s} + \frac{R_\mathrm{a}^\mathrm{c}}{1+R_\mathrm{a}^\mathrm{c}C_\mathrm{dl}^\mathrm{c}s}$ | |
| B: | $h(s) = \frac{R_\mathrm{a}^\mathrm{a}}{1+R_\mathrm{a}^\mathrm{a}C_\mathrm{dl}^\mathrm{a}s} \cdot \frac{R_\mathrm{a}^\mathrm{c}}{1+R_\mathrm{a}^\mathrm{c}C_\mathrm{dl}^\mathrm{c}s}$ | |
| C: | $h(s) = (R_\mathrm{a}^\mathrm{a} + R_\mathrm{a}^\mathrm{c}) \frac{1+\left(C_\mathrm{dl}^\mathrm{a}+C_\mathrm{dl}^\mathrm{c}\right)s}{\left(1+R_\mathrm{a}^\mathrm{a}C_\mathrm{dl}^\mathrm{a}s\right)\left(1+R_\mathrm{a}^\mathrm{c}C_\mathrm{dl}^\mathrm{c}s\right)}$ | |
| D: | $h(s) = (C_\mathrm{dl}^\mathrm{a} + C_\mathrm{dl}^\mathrm{c}) \frac{R_\mathrm{a}^\mathrm{a}R_\mathrm{a}^\mathrm{c}+(R_\mathrm{a}^\mathrm{a}+R_\mathrm{a}^\mathrm{c})s}{\left(1+R_\mathrm{a}^\mathrm{a}C_\mathrm{dl}^\mathrm{a}s\right)\left(1+R_\mathrm{a}^\mathrm{c}C_\mathrm{dl}^\mathrm{c}s\right)}$ | |

▲

Figure 10 shows the step-response in combined activation voltage $u_\mathrm{a} = u_\mathrm{a}^\mathrm{a} + u_\mathrm{a}^\mathrm{c}$ after a step change in $i''$; note that $i'' \propto i_\mathrm{c}$. NOTE! Different activation voltage models (Butler-Volmer) may give quite different (e.g., 10 times slower) time responses.

**Problem 16.** Electrodynamics — time constant

Based on Fig. 10, give an estimate of the time constant $T_\mathrm{e}$ of the electric (sub-) system.

| | **Problem 16:** The time constant $T_\mathrm{e}$ of the electric subsystem is — which answer is ***correct***? | Choice |
|---|---|---|
| A: | The variation in $u_\mathrm{a}$ is too small to determine the time constant | |
| B: | $T_\mathrm{e} = 4\,\mathrm{ms}$ | |
| C: | $T_\mathrm{e} = 2\,\mathrm{ms}$ | |
| D: | $T_\mathrm{e} = 0.5\,\mathrm{ms}$ | |

In a stack of $N_c$ cells, the stack transfer function $h_s(s)$ will be

$$h_s(s) \propto \frac{1}{(1 + T_e s)^{N_c}}. \tag{53}$$

It is of interest to consider whether this "cascade" of $N_c$ transfer functions, each of form $\frac{1}{1+T_e s}$, results in a significant overall dynamic effect. For such an assessment, we consider the following exponential function, $\exp(\tau s)$:

$$\exp(\tau s) = \exp\left(n\frac{\tau}{n}s\right) = \left(\exp\left(\frac{\tau}{n}s\right)\right)^n. \tag{54}$$

With large $n$, $\tau/n$ is small, and we have

$$\exp\left(\frac{\tau}{n}s\right) \approx 1 + \frac{\tau}{n}s$$
$$\Downarrow$$
$$\exp(\tau s) \approx \left(1 + \frac{\tau}{n}s\right)^n. \tag{55}$$

For linear systems, a transfer function $\exp(-\tau s) = 1/\exp(\tau s)$ describes a time delay of size $\tau$.

**Problem 17.** Electrodynamics of stack

Use these considerations (Eqs. 53–55) to find an approximation to the transfer function $h_s(s)$.

| | **Problem 17:** Which approximate expression for the transfer function from $i''(s)$ to $u_a(s)$, denoted $h_s(s)$, is ***correct***? | Choice |
|---|---|---|
| A: | $h_s(s) \propto \exp(N_c T_e s)$ | |
| B: | $h_s(s) \propto \exp\left(\frac{T_e}{N_c}s\right)$ | |
| C: | $h_s(s) \propto \exp(-N_c T_e s)$ | |
| D: | $h_s(s) \propto \exp\left(-\frac{T_e}{N_c}s\right)$ | |

Figure 11 shows the step-response in a normalized activation voltage $u_a = u_a^a + u_a^c$ cascaded through $N_c$ cells after a step change in $i''$, scaled to $1\,\text{V}$ for numerical reasons. This provides a quantitative measure to assess the importance of including the electrodynamics in the PEM electrolyzer model.

**Problem 18.** Electrodynamics importance

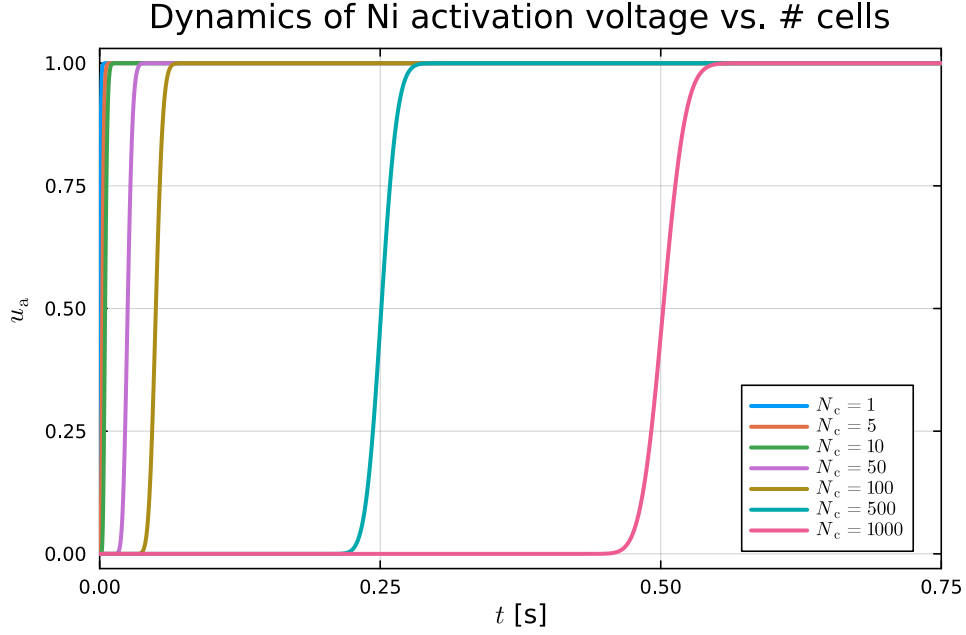Assess the importance of including electrodynamics in the model.

Figure 11: Case of $N_c$ cascaded cells: total (normalized) activation voltage $u_a$ after a step change in current density $i''$.

| | **Problem 18:** Which of the following statements is ***correct***? | Choice |
|---|---|---|
| A: | With $T_e \approx 0.5\,\text{ms}$, the electric time constant is never relevant, and we can safely neglect the dynamics of the electric subsystem. | |
| B: | For unrealistically large values of $N_c$ ($N_c$ in the order of 1000), the electric time delay approaches the fast dynamics of gas pressures. Because there is considerable uncertainty in the electric time constant, the need to include an electric model should still be re-assessed depending on an improved activation voltage model (Butler-Volmer) and for the actual number of cells $N_c$ in series. | |
| C: | Because the dynamics of the water levels are so slow, the electric time constant is never relevant, see Eq. 29. | |
| D: | There is no disadvantage in including the electric time constant, so we should always do that. | |

▲

## 1.7 Electrolyzer efficiency

Three common measures of electrolyzer efficiency are:

**LHV efficiency:** The lower heating value (LHV) efficiency $\eta_\ell$ is defined as

$$\eta_\ell \triangleq \frac{u_n}{u_c} \tag{56}$$

where $u_n$ is the equilibrium (Nernst) voltage $u_n = \frac{\Delta_r \tilde{G}}{\nu_{e^-} F}$ at the operating temperature and pressures, and $u_c$ is the cell voltage at the operating temperature, pressures, and current density $i''$.

**HHV efficiency:** The higher heating value (HHV) efficiency $\eta_h$ is defined as

$$\eta_h \triangleq \frac{u_{th}}{u_c} \tag{57}$$

where $u_{th}$ is the thermoneutral voltage at the operating temperature and pressures, and $u_c$ is the cell voltage at the operating temperature, pressures, and current density $i''$.

**Production efficiency:** The production efficiency is defined as the supplied electric power $\dot{W} = u_s i_s = N_c u_c i_c$ per hydrogen production $\dot{m}_{H_2}$,

$$\varepsilon_p = \frac{\dot{W}}{\dot{m}_{H_2}} = \frac{N_c u_c i_c}{\dot{m}_{H_2}} = \frac{N_c A_c u_c i''}{\dot{m}_{H_2}}. \tag{58}$$

Observe that contrary to $\eta_\ell$ and $\eta_h$, $\varepsilon_p$ has dimension; $\varepsilon_p$ is often given in units kW/ (kg/h) = kWh/kg.

**Problem 19.** Energy efficiency

Assume the following values taken from the group project: $\dot{m}_{H_2}^{max} = 24\,\text{kg/h}$, $i''_{max} = 2\,\text{A/cm}^2$, $A_c = 160\,\text{cm}^2$, $N_c = 2000$, $u_c = 2.5\,\text{V}$, $u_n \approx 1.25\,\text{V}$ (Fig. 4, $T = 60\,°\text{C}$, $p_{H_2} = 30\,\text{bar}$), $u_{th} \approx 1.49\,\text{V}$ (Fig. 7). Find the three efficiencies $\eta_\ell$, $\eta_h$, and $\varepsilon_p$.

| | **Problem 19:** The energy efficiencies are — which statement is **correct**? | Choice |
|---|---|---|
| A: | $\eta_h = 0.4$, $\eta_\ell \approx 0.5$, $\varepsilon_p \approx 50\,\text{kWh/kg}$ | |
| B: | $\eta_\ell = 0.4$, $\eta_h \approx 0.5$, $\varepsilon_p \approx 50\,\text{kWh/kg}$ | |
| C: | $\eta_h = 0.5$, $\eta_\ell \approx 0.6$, $\varepsilon_p \approx 67\,\text{kWh/kg}$ | |
| D: | $\eta_\ell = 0.5$, $\eta_h \approx 0.6$, $\varepsilon_p \approx 67\,\text{kWh/kg}$ | |

▲

**Problem 20.** Energy efficiency range

Consider the HHV efficiency, the high heating value efficiency $\eta_h$. What is the possible *range* of $\eta_h$ at the operating conditions (given temperature and pressures) of the group project when the current density $i''$ is allowed to change?

| | **Problem 20:** The range of the HHV efficiency with varying $i''$ is approximately — which statement is **correct**? | Choice |
|---|---|---|
| A: | $\eta_h \in [0, 1]$ | |
| B: | $\eta_h \in [0, 1.2]$ | |
| C: | $\eta_h \in [-0.2, 1]$ | |
| D: | $\eta_h \in [0.2, 1]$ | |

▲

— **END OF EXAM** —