



Report

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Title

Dynamic modeling of a system of electrolyzers

Summary

This work presents dynamic model for hydrogen electrolyzer plant. The model is implemented in MATLAB using CasADi symbolic framework. Model simulations are performed to predict system behaviour with intermittent power supply. The developed model is intended to be further used for control and optimization studies for hydrogen production using system of alkaline water electrolyzers.

Conclusion

The results of electrolyzer from the developed model simulation are in accordance to the prediction from Ulleberg's model [4].

The results for compressor and gas storage system also corroborate to our understanding of physical system behavior.

Recommendation

Recommendation for further studies on the developed dynamic hydrogen electrolyzer plant model is summarized below:

- The assumption that temperature of all electrolyzers is same can be removed for the fact that material properties of each individual electrolyzer can be different which may lead to different thermal performances. Modifying current model to include this will need a separate heat balance per electrolyzer to be established and an additional model for lye circulation system. Doing this will make electrolyzer model more realistic and will certainly improve the robustness of the dynamic model.
- The most challenging part with the use of renewable power is to handle the involved intermittencies. Therefore, designing a robust control structure is at the very core for successful implementation of this concept at plant scale. Control system design studies can be performed using this model. A comprehensive study on different possible control structures will help to identify manipulated variables and the controlled variable that need to be stabilized.
- During operation the behavior of each individual electrolyzer in the system will be different after a certain time. The performance characteristics will be different for each electrolyzer, that is when the power distribution to each electrolyzer out of the total available power becomes more involved. This calls for the formulation of an optimization problem to maximize the total hydrogen production based on the individual electrolyzer performance and the total power.

Key words

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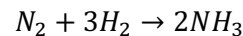
1 Introduction

This section gives background for this project. The process for production of green fertilizers is described and previous work in alkaline electrolysis is introduced, along with the scope of this work.

1.1 Background

Ammonia is one of the basic chemicals to produce nitrogenous fertilizers. Approximately 88% of ammonia [1] produced globally is used as fertilizers which are crucial for feeding the planet.

Industrially, ammonia is produced via the Haber Bosch process which requires hydrogen and nitrogen in the ratio 3:1 at moderately elevated temperature (450 °C) and high pressure (100+ bar).



The nitrogen is extracted from air and hydrogen is currently obtained by steam-methane reforming of natural gas.

Steam-methane reforming of natural gas to get hydrogen for ammonia production is fundamental to produce fertilizer and contributes to around 2% of the world greenhouse gas emissions [2]. Therefore, to make fertilizer industry more sustainable and greener it is important to look for the ways of obtaining hydrogen from carbon free sources.

1.2 Green Fertilizer Production

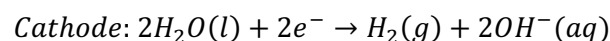
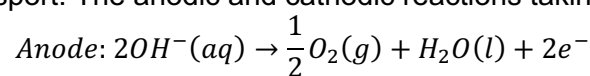
Green fertilizer production refers to the production of fertilizers from sustainable sources to reduce the carbon footprint of chemical industry. The core technology for this consists of finding ways to produce green hydrogen.

Water electrolysis using renewable power to generate hydrogen is the most promising option that will help to eliminate the dependence on fossil fuel-based sources. The main water electrolysis technologies present today are alkaline water electrolysis (AEL), proton exchange membrane electrolysis (PEMEL) and solid oxide electrolysis (SOEL).

Alkaline water electrolysis (AEL) is most mature and commercially available electrolysis technology [3]. It has been around for over a century and that is why the first step in making fertilizer industry greener is to make the production of hydrogen from alkaline water electrolysis industrially profitable.

1.2.1 Technology: Alkaline water electrolyzer

The decomposition of water into hydrogen and oxygen can be achieved by passing an electric current (DC) between two electrodes separated by an aqueous electrolyte with good ionic conductivity. In an alkaline electrolyzer, the electrolyte is usually aqueous potassium hydroxide (KOH), where the potassium ion K^+ and hydroxide ion OH^- take care of the ionic transport. The anodic and cathodic reactions taking place here are



Operating temperature is set mainly between 70-100 °C and operating pressure is between 1 and 30 bars. [4]

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The electrodes are immersed in an alkaline aqueous solution with weight concentration (20-30 wt.%) and therefore they must be corrosion resistant, have good electrical conductivity and catalytic properties, allowing better electrochemical transfer.

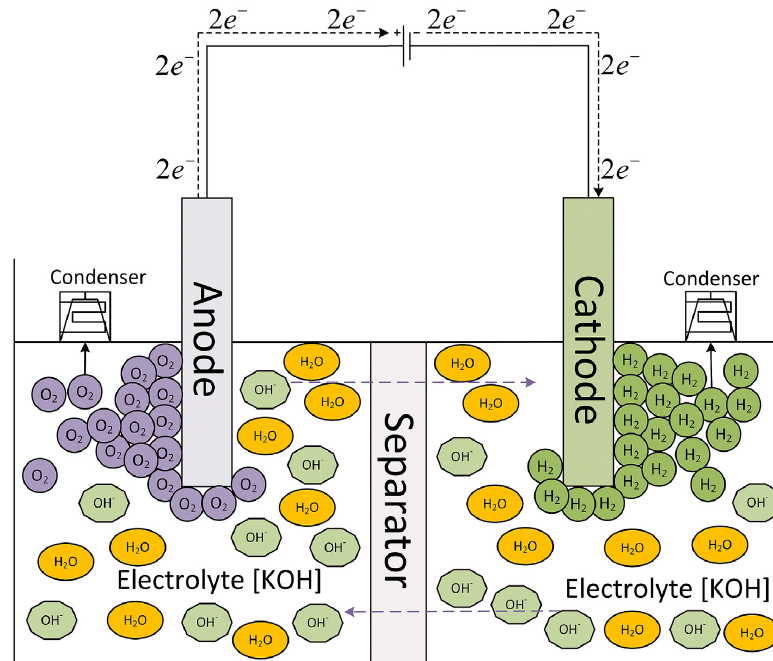


Figure 1: Schematic of the alkaline electrolyser cell

Physically an electrolyzer consists of several cells. There are two electrolysis cell configurations based on how these cells are connected namely, monopolar and bipolar cell configuration.

In monopolar configuration, each cell is connected in parallel to form large module of electrolysis stack. Hence, the voltage between individual pair of cells is directly equal to the total cell voltage and the sum of cell current is equal to the total cell current. In this configuration, diaphragm separates the anodic and cathodic sections and the electrode is located in each section. Therefore, same electrochemical reaction (reduction/oxidation) occurs on both sides of each electrode.

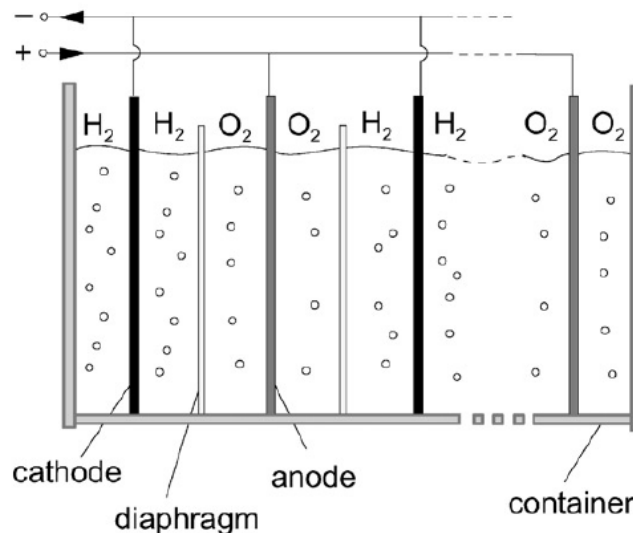


Figure 2: Principle of monopolar electrolyser design [4]

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In bipolar design, each cell is connected in series to form large module of electrolysis stack. Hence, the cell current is directly equal to the current which is passed through each individual cell and the sum of voltages between individual pairs is equal to the total cell voltage. Bipolar plate separate individual cells in this configuration. This bipolar plate acts as anode for one cell and as cathode for the other cell. Therefore, two different electrochemical reaction occurs on both sides of each bipolar plate.

Most commercial alkaline electrolyzers today are bipolar as they are more compact, gives shorter current paths in electrical wires and electrodes and has better electrolyzer efficiency. However, there are also some disadvantages with the bipolar designs like, parasitic currents which are generated in the cell because of movement of the ions in the migration electric field and can cause corrosion problems.

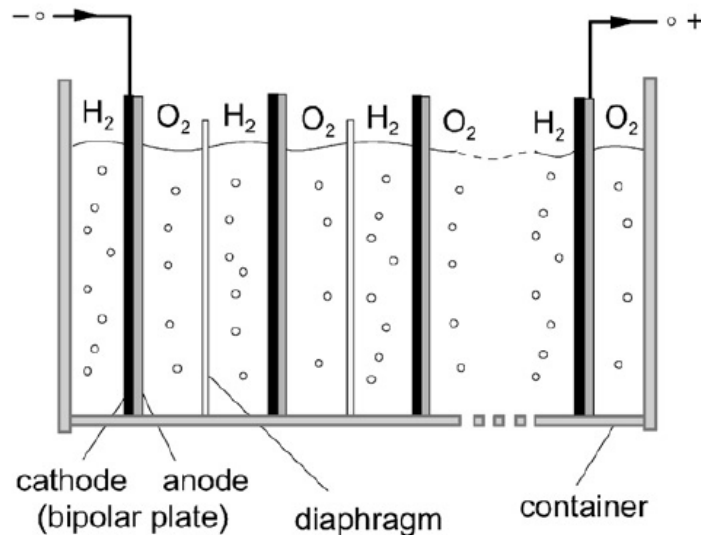


Figure 3: Principle of bipolar electrolyser design [4]

In the case of atmospheric electrolyzers, a compressor unit is required to increase the pressure before storing the hydrogen produced. Operation at higher pressure would overcome the compression step and increase overall efficiency. Electrolyzers operated at either atmospheric pressure or at the pressure up to 30 bar represent the current state of the art with regard to the product gas pressure.

Here we have discussed the standalone operation of alkaline electrolyzers and we disregard any coupling to the power source (like one in [5] where direct coupling of alkaline electrolyser cell and PV module is discussed).

1.3 Scope of Work

The scope of this work is to develop a dynamic model for alkaline water electrolysis plant to produce hydrogen. The model is to be implemented in MATLAB using CasADi symbolic framework. The model will be solved using the numerical integrator IDAS, available in open-source software SUNDIALS suite, and simulation of different scenarios for operation of this dynamic system of electrolyzers will be performed.

This work assumes usage of renewable power sources to provide electricity for electrolysis. These sources, are intermittent in nature and that's why the model developed should be robust to predict all the system property. The model is intended to

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be further used for control and optimization studies for hydrogen production using system of alkaline water electrolyzers.

1.4 Previous Work

There are different approaches to the dynamic modelling of alkaline electrolyzers. The model by Ulleberg [4] is based on a combination of fundamental thermodynamics, heat transfer theory, and empirical electrochemical relationships. This model can be used to predict the cell voltage, hydrogen production, efficiencies, and operating temperature and is the most widely used model in the literature for dynamic modelling of alkaline electrolyzers.

The research article by D. Martinez et.al. [5] discusses a MATLAB/Simulink/Simscape power system implementation of an alkaline electrolyzer directly coupled to a photovoltaic module. In addition to the steady state output, boundary conditions are applied to the Ulleberg's models [4] to include the transient performance.

Most relevant electrolyzer model from 1990s is SIMELINT-program [6]. This program which was validated against measured data, accurately predicts the thermal behaviour, cell voltage, gas purities, and efficiencies for any given power or current profile.

[7] presents a multi-physics model used for the design and diagnosis of the alkaline electrolyzers. The model considers the variation of all structural parameters (geometry, materials and their evolution depending on operating conditions) and operational parameters of the electrolyzer (temperature, pressure, concentration, bulk bubbling and recovery rate of electrode surface by the bubble), while the models in [4] involve only the temperature.

In continuation to the work presented in [7], C. Henao et al. have proposed an Alkaline Electrolyser Simulation Tool (AEST) [8] based on a physics model with an electrical analogy in order to emulate the physical and electrical behaviour of the alkaline electrolyser. This paper discusses the power electronics involved in alkaline electrolyzer and simulation results using MATLAB/Simulink/SimPowerSystems® for electrolyser start-up phase and steady state operation are also presented.

Casual ordering graph (COG) is a proposition of symbolism for transcribing thought which helps to describe dynamic systems in a physical and unambiguous manner. This approach is used to illustrate the global schemes for modelling of the electrolyzer, as well as utilities (i.e. compressor) and hydrogen storage tank in [9]. This research article discusses the control oriented electrolyzer model which is again based on Ulleberg's model [4]. However unlike [4], the thermal model is replaced by a constant external temperature which can be set.

In most applications, the hydrogen from alkaline electrolysis is needed to be at higher pressures (like fuel cell electric vehicles). The power required for high pressure water electrolysis, wherein water is pumped to higher pressure may be less than the power required for atmospheric water electrolysis wherein the pressure of produced gaseous hydrogen is compressed, since the pump power for water is much less than that for hydrogen gas. In the study done in [10], the ideal water electrolysis voltage up to 70 MPa and 250 °C, is estimated by referring to both the results of LeRoy et al. [11] up to 10 MPa and 250 °C, and the latest steam tables. The study concluded that using high-pressure water electrolysis, the power required to produce high pressure hydrogen by water electrolysis is estimated to be about 5% less than that required for atmospheric water electrolysis, assuming compressor and pump efficiencies of 50%.

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Interestingly, the modelling and control of alkaline electrolyzer can also be done using data driven approach for system identification as discussed in [12]. The electrolysis process model was developed using a nonlinear identification technique based on Hammerstein structure. The electrochemical electrolysis was carried out in an electrolyzer composed of 12 series connected steel cells with a 30 wt.% solution of KOH. Model Predictive Control (MPC) is used to control the energy consumption of the developed electrolyzer.

The hydrogen production, storage and conversion subsystems are studied in detail in [13]. A comprehensive mathematical model for hydrogen storage is derived to get a closer insight into the total system efficiency and different loss mechanisms. This research is originally intended to study the seasonal storage of hydrogen from a small self-sufficient solar hydrogen pilot plant at Helsinki University of Technology. The concepts discussed in this article can be extended to present work on the pressurized hydrogen storage.

A system of alkaline electrolyzers is investigated in [14]. Experimental measured data from a 150-kW alkaline water electrolyzer is used for the development of a simulator model.. The prediction of the temperature and efficiency for the different scales of electrolyzers (1MW and 5MW) was done using the developed model to investigate performance with regard to large scale hydrogen production. The two larger electrolyzers were not actual systems and they were only considered for simulation purposes. The performance of the combination of large and small electrolyzers was predicted and compared.

The discussion on the product gas purity in alkaline water electrolysis is presented in [15]. The model described in this article presents the electrolysis cell through coupled continuously stirred tank reactors and mass transfer phenomena between the phases are explained through the application of Reynolds and Sherwood correlations.

A review on the status of water electrolysis for energy system is presented in [3]. This review provides necessary understanding of electrolysis fundamentals and technologies for techno-economic analysis of water electrolysis-based concepts. It compares the alkaline electrolysis (AEL), PEM electrolysis (PEMEL) and solid oxide electrolysis (SOEL) in terms of available capacity, nominal and part load performance, flexibility, lifetime and investment costs. It concludes that the AEL is the most mature technology and can be adapted most easily to the present requirements.

2 Model development

In this section, the development of model is described. Detailed electrolyzer plant flowsheet is introduced first to give an overview of the hydrogen production plant using alkaline water electrolysis.

The model developed in this work focuses on the three basic sub domains of the electrolyzer plant, i.e. electrolyzer stacks, compressor and the gas storage. The model has flexibility of selecting number of electrolyzers and power supply for each one of them. The dynamic model simulation is initialized using the steady state solution. It is assumed that the temperature of the circulating lye solution at steady state operation is 80 °C. CasADi framework is used for the symbolic modeling in MATLAB. The system of Differential-Algebraic Equations (DAE) is solved using numerical integrator IDAS, available in the open-source software SUNDIALS suite. The MATLAB code is included in Appendix.

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2.1 Detailed Plant Flowsheet

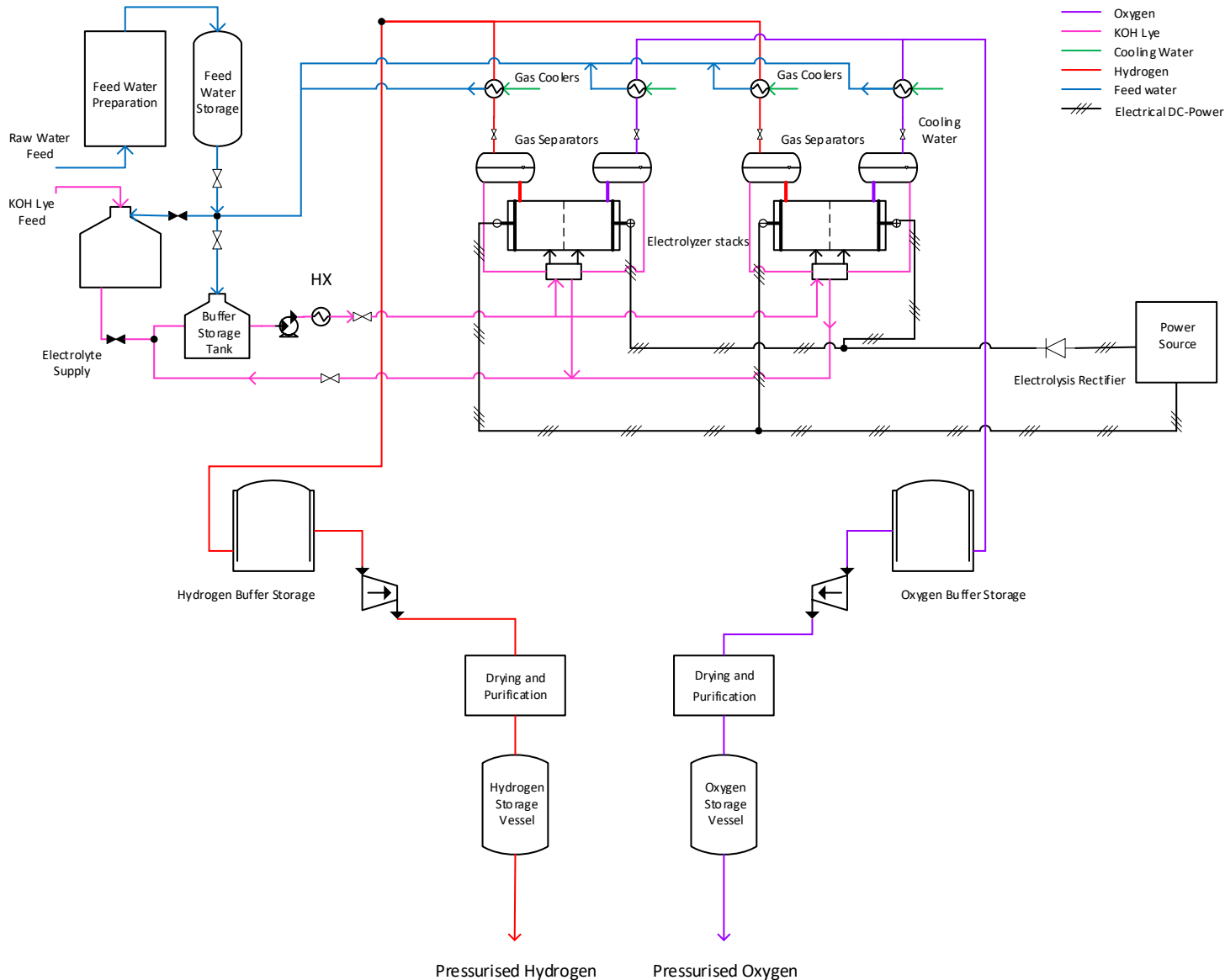


Figure 4: Flowsheet of hydrogen production plant from alkaline water electrolysis

As shown in Figure 4 above, the hydrogen electrolyser plant consists of following basic sections:

- Electric power supply: Water electrolysis requires direct current supply; therefore, it is necessary to convert the normal alternating current from power source to direct electric supply using rectifier.
- The electrolyser stacks: Water splitting reaction to hydrogen and oxygen is carried out in the series of electrolyzers stacked together.
- Gas separators and coolers: The produced gases (H_2 & O_2) are separated from lye solution and cooled before they are processed further for storage.
- Lye/Water circulation system: This system includes auxiliary equipment needed for separation and circulation of lye and water like heat exchangers, pumps, water purification and pumping, valves and control system.
- Gas purification and storage: The produced hydrogen and oxygen are dried and compressed using pump before they are sent to pressurised storage vessels.

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The renewable power source provides direct supply to the stack of electrolyzers. Electrolyzer stack receives alkaline water feed, and electrolysis is carried out in this stack. The evolved hydrogen and oxygen from the cathodic and anodic compartment is separated from lye solution and cooled in gas separator and cooler located downstream of the electrolyzers. The collected liquid lye solution from gas separators is mixed and recirculated through the electrolyzer stack. This recirculation involves auxiliary operations like pumping and heat exchange with the cooling water before lye solution is sent again to the electrolyzers. The evolved gases from electrolyzers are collected in a buffer storage tank after which they are dried and purified to desired level before being compressed for storage to high pressure tanks.

2.2 Simplified Flowsheet

The simplified flowsheet of the electrolyzer system investigated in this work is shown in Figure 5. The alkaline electrolysis plant considered in our study consists of 3 sub domains, i.e. electrolyzer, compressor and gas storage. The following sections will describe the model equations and assumptions considered when modeling each of these domains.

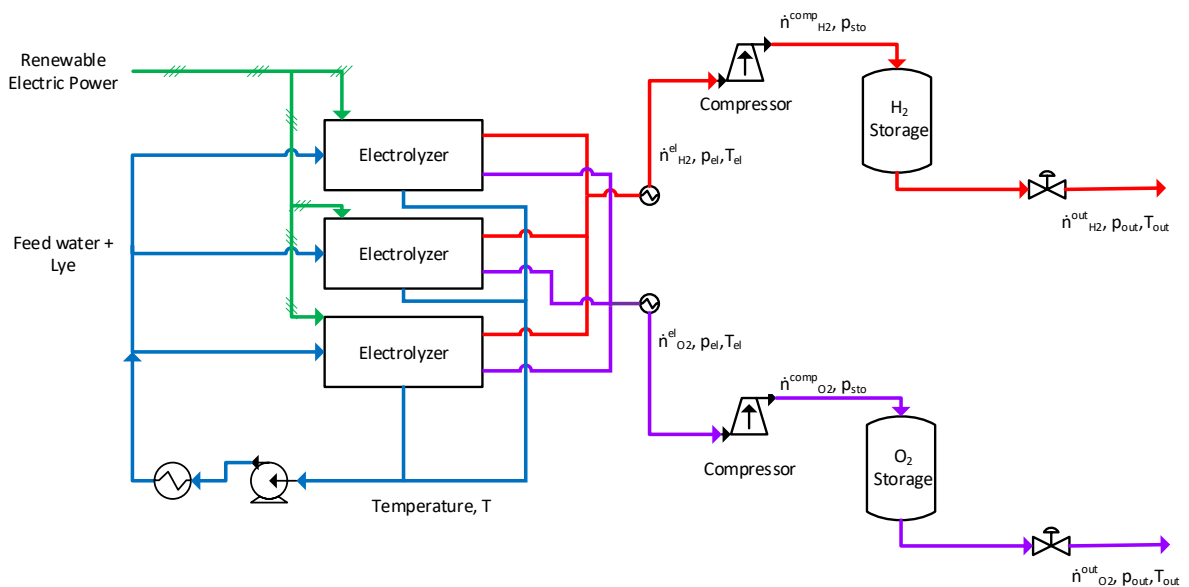


Figure 5: Flowsheet of simplified alkaline electrolysis plant

2.3 Electrolyzer

A complete description of alkaline electrolyzer requires descriptions of interconnecting domains such as thermodynamic, electrochemical and thermal effects. Here, we have used Ulleberg's model [4] to define these effects.

2.3.1 Thermodynamic model

Thermodynamics provides a framework for describing reaction equilibrium and thermal effects in electrochemical reactors. It also provides basis for defining the driving forces for transport phenomena in electrolytes and led to the description of the properties of

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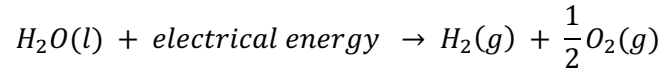
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electrolyte solutions. In Ulleberg's model, maximum electrolyzer temperature of 100°C is assumed.

In alkaline electrolysis the total reaction for water splitting is:



Following assumptions can be made about above reaction, [4]:

- Hydrogen and oxygen are ideal gases
- Water is an incompressible fluid
- The gas and liquid phases are separate

Based on these assumptions the total change in enthalpy ΔH , for splitting water is the enthalpy difference between the products and reactants. This is also true for the change in entropy ΔS .

The change in Gibbs energy ΔG , is expressed by

$$\Delta G = \Delta H - T\Delta S$$

At standard conditions (25°C and 1 bar) the change in Gibbs energy is positive as the splitting of water is non-spontaneous. The standard Gibbs energy for water splitting is $\Delta G^\circ = 237 \text{ kJ mol}^{-1}$. For an electrochemical process operating at constant pressure and temperature the maximum possible useful work (i.e. the reversible work) is equal to the change in Gibbs energy ΔG . Faraday's law relates the electrical energy (emf) needed to split water to the chemical conversion rate in molar quantities. The emf for a reversible electrochemical process, or the reversible cell voltage, is expressed by

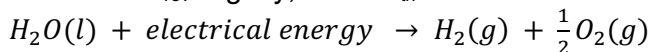
$$U_{rev} = \frac{\Delta G}{zF}$$

The total amount of energy needed in water electrolysis is equivalent to the change in enthalpy ΔH . The change in Gibbs energy ΔG , includes thermal irreversibilities $T\Delta S$, which is equal to heat demand for a reversible process. The standard enthalpy for water splitting is, $\Delta H^\circ = 286 \text{ kJ mol}^{-1}$. The cell voltage at which the supplied electrical energy participates both in ΔG & $T\Delta S$, and there is no heat generation or heat absorption from outside of the system is referred to as thermoneutral cell voltage.

The total energy demand ΔH is related to the thermoneutral cell voltage by the expression

$$U_{tn} = \frac{\Delta H}{zF}$$

At standard conditions $U_{rev}=1.229 \text{ V}$ and $U_{tn}=1.482$, but these will change with temperature and pressure. In the applicable temperature range, U_{rev} decreases slightly with increasing temperature, while U_{tn} remains almost constant. Increasing pressure increases U_{rev} slightly, while U_{tn} remains constant.



2.3.2

Electrochemical model

The electrode kinetics is modeled using empirical current-voltage (I-U) relationships [4]. The cell voltage is always higher than reversible cell voltage because of irreversibilities. These irreversibilities leads to extra voltage in the cell, which is called overvoltage. This overvoltage is composed of ohmic, diffusion and activation voltages.

The basic form of I-U curve as given in [4] is used here

$$U = U_{rev} + \frac{r_1 + r_2 T}{A} I + \log_{10} \left(\frac{t_1 + \frac{t_2}{T} + \frac{t_3}{T^2}}{A} I + 1 \right)$$

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This temperature dependent I-U model has been proposed by Ulleberg, [4]. Here, r_1 & r_2 are ohmic resistance parameters, s , t_1 , t_2 & t_3 are overvoltage coefficients and A is the electrode area.

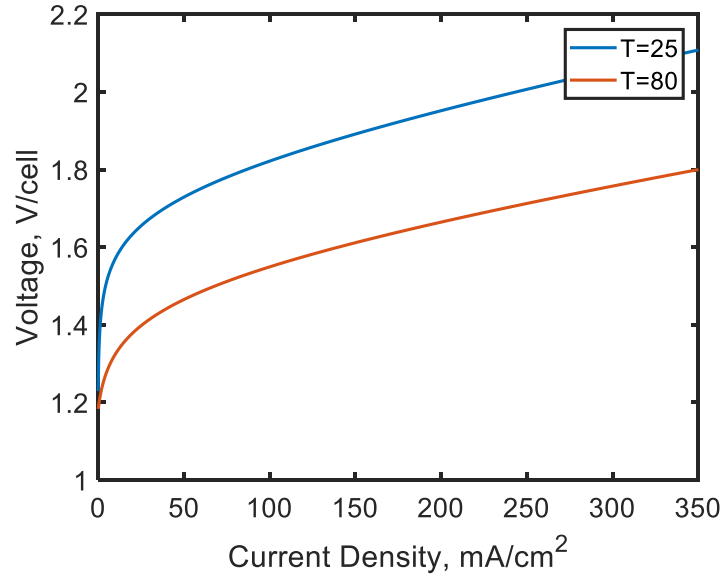


Figure 6: Typical I-U curve for an electrolyzer

Faraday efficiency is defined as the ratio between the actual and theoretical maximum amount of hydrogen produced in an electrolyzer. Faraday efficiency is caused by the parasitic current losses and the contamination of electrolyte because of dissolution of H_2 in O_2 . The fraction of parasitic currents to total current increases with decreasing current densities. Also, an increase in temperature will reduce resistance that increases parasitic current and lowers Faraday efficiency. An empirical relation given in [4] by Ulleberg accurately depicts this phenomena for a given temperature as

$$\eta_F = \frac{\left(\frac{I}{A}\right)^2}{f_1 + \left(\frac{I}{A}\right)^2} f_2$$

Here, f_1 & f_2 are parameters related to Faraday efficiency. According, to Faraday's law hydrogen production rate in an electrolyzer cell is proportional to transfer rate of electrons at the electrodes, which in turn is equivalent to the electrical current in the external circuit. Hence, hydrogen production rate in an electrolyzer which consists of several cells connected in series, is given as

$$\dot{n}_{H_2} = \eta_F \frac{n_e I}{zF}$$

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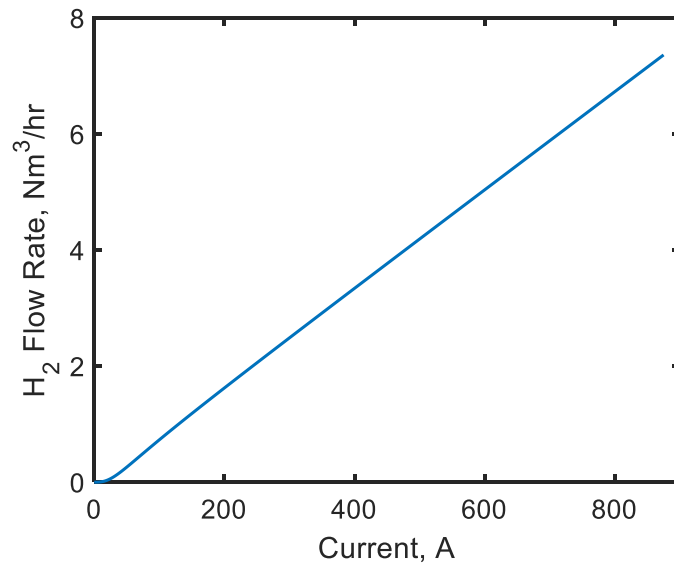


Figure 7: H_2 production rate as a function of electrical current.

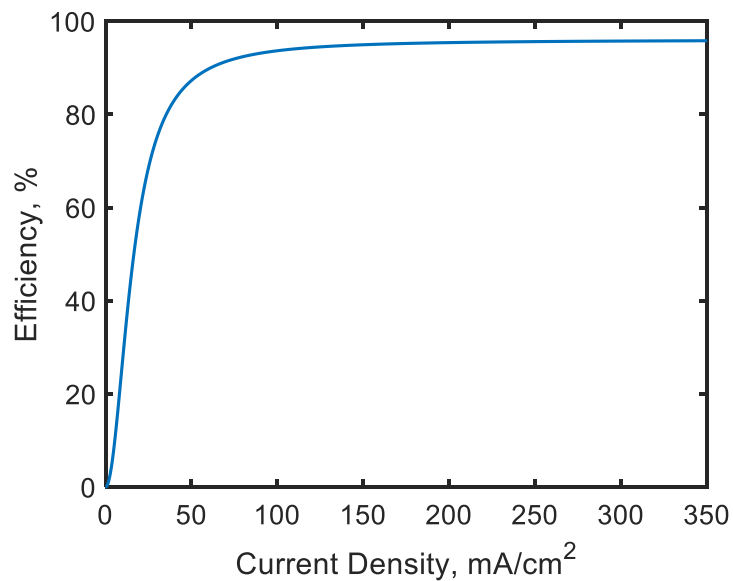


Figure 8: Faraday efficiency for PHOEBUS electrolyzer,

Figure 7 and Figure 8 shows Hydrogen production as a function of measured electric current and Faraday efficiency as a function of current density for a certain electrolyzer. These graphs are obtained by modeling the electrochemical reactions in MATLAB and agrees to the results published in Ulleberg's study [4].

The energy efficiency for an alkaline electrolyzer can be calculated from the thermoneutral voltage and the cell voltage by the expression

$$\eta_e = \frac{U_{tn}}{U}$$

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2.3.3 Thermal model

The thermal balance for an electrolyzer using lumped thermal capacitance model can be written as

$$C_t \frac{dT}{dt} = \dot{Q}_{gen} - \dot{Q}_{loss} - \dot{Q}_{cool}$$

where

$$\dot{Q}_{gen} = n_c (U - U_{tn}) I$$

\dot{Q}_{gen} is internal heat generation when the electrolyzer is operated at voltages above thermoneutral voltage. Here, C_t is overall thermal capacity of the electrolyzer.

$$\dot{Q}_{loss} = \frac{T - T_a}{R_t}$$

\dot{Q}_{loss} is the total heat loss to the ambient and is calculated using convective cooling relationship, where R_t is the overall thermal resistance of the electrolyzer. Net internal heat generated and heat loss of the whole electrolyzer stack is the sum of contribution from each individual electrolyzer.

\dot{Q}_{cool} is the auxiliary cooling demand. At steady state,

$$\dot{Q}_{cool} = \dot{Q}_{gen} - \dot{Q}_{loss}$$

Before we proceed to solve the above thermal equations, it is to be noted that here we have assumed all the electrolyzers to be operating at the same temperature, which is equal to the temperature of the circulating lye.

The dynamics of the thermal model given above is dependent on the thermal time constant, τ_t which is defined as

$$\tau_t = C_t R_t$$

2.4 Compressor

The hydrogen from the atmospheric electrolyzer is atmospheric pressure and therefore, a compressor is needed to compress hydrogen to high pressure storage tank. The compressors available in process industry today can be categorized in two distinct categories: reciprocating and rotary compressors.

The choice of a compressor for electrolyzer is based on the size of the operation. For pilot plant scale, positive displacement compressor is suggested whereas for larger full plant scale operation centrifugal compressor is the ideal choice (as suggested by Pieter Van Driessche).

The calculation of the performance of centrifugal compressors is based on a polytropic compression step. The polytropic process is expressed as

$$PV^k = \text{constant}$$

where, k denotes the polytropic exponent and P , V represents pressure and volume of the process. This polytropic compression describes the actual process involving both heat transfer and friction happening within the compressor.

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The relationship between molar flowrate of hydrogen out of the compressor, $\dot{n}_{H_2}^{comp}$ and compressor power is [9]:

$$\dot{n}_{H_2}^{comp} = \frac{\alpha}{w} Power_{comp} \quad 1$$

and

$$w = \frac{kRT_{el}}{k-1} \left[\left(\frac{p_{sto}}{p_{el}} \right)^{\frac{k-1}{k}} - 1 \right] \quad 2$$

where w is the polytropic work, α is the compressor efficiency, $Power_{comp}$ is compressor power, T_{el} is inlet gas temperature to the compressor, p_{el} is inlet gas pressure corresponding to the pressure of hydrogen pressure in the electrolyzer, p_{sto} is the outlet gas pressure corresponding to the hydrogen pressure in the storage tank and R is the gas constant.

Here it is assumed that $\dot{n}_{H_2}^{comp}$ is equal to the flowrate of hydrogen out from electrolyzer, $\dot{n}_{H_2}^{el}$.

Combining 1 & 2, solving for $Power_{comp}$ we get

$$Power_{comp} = \frac{\dot{n}_{H_2}^{comp}}{\alpha} \frac{kRT_{el}}{k-1} \left[\left(\frac{p_{sto}}{p_{el}} \right)^{\frac{k-1}{k}} - 1 \right] \quad 3$$

A centrifugal compressor is a type of rotary compressor and has fixed pressure ratio, therefore $Power_{comp}$ is a dependent variable that we will solve for.

As given in [16] the polytropic exponent is related to adiabatic component γ , through polytropic efficiency E_p as,

$$\frac{k-1}{k} = \frac{\gamma-1}{\gamma} \frac{1}{E_p} \quad 4$$

The polytropic efficiency of the centrifugal compressor is between 0.7 – 0.75 as mentioned in [16]. For our calculations here, we will assume $E_p = 0.75$. The adiabatic exponent γ for hydrogen, i.e. a diatomic molecule is 1.4. Using the relation in 4 we get polytropic exponent $k = 1.62$.

2.5 Gas Storage

2.5.1 Hydrogen storage

The overall mole balance of a gas storage, as shown in Figure 5 can be expressed as

$$\frac{dn_{sto}}{dt} = \dot{n}_{H_2}^{comp} - \dot{n}_{H_2}^{out} \quad 5$$

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where n_{sto} is the molar hold-up and $\dot{n}_{H_2}^{out}$ is the molar outlet flow. After inserting the ideal gas law $n = PV/RT$ the equation becomes

$$\frac{dp_{sto}}{dt} = \frac{(T_{sto} + 273.15)R}{V_{sto}} (\dot{n}_{H_2}^{comp} - \dot{n}_{H_2}^{out}) \quad 6$$

where V_{sto} is the storage volume, T_{sto} is the storage temperature and R is the gas constant. The operating pressure storage p_{sto} is the dynamic state variable.

The outlet molar flow is given by the valve equation

$$\dot{n}_{H_2}^{out} = k_{vlv} z \sqrt{p_{sto} - p_{out}} \quad 7$$

Here k_{vlv} is the valve constant and z is the valve displacement.

The storage temperature T_{sto} is assumed to be ideally controlled to 25 °C. The pressure of the electrolyzer is assumed to be constant. The pressure in the vessel increases as it is filled with more gas. However, the pressure of the inlet stream does not change. Note that the pressure of the inlet stream must be higher than the storage pressure in order to get it into the storage.

2.5.2 Oxygen storage

The oxygen production is calculated directly from the stoichiometry of the electrolysis reaction.

$$\dot{n}_{H_2}^{el} = \dot{n}_{H_2O}^{el} = 2\dot{n}_{O_2}^{el}$$

The overall mole balance for oxygen gas storage is given by eq. (5), and assuming ideal gas behaviour the equation becomes

$$\frac{dp_{sto}}{dt} = \frac{(T_{sto} + 273.15)R}{V_{sto}} (\dot{n}_{O_2}^{comp} - \dot{n}_{O_2}^{out})$$

There is no accumulation of gases in the compressor, therefore $\dot{n}_{O_2}^{comp} = \dot{n}_{O_2}^{el}$. Like the hydrogen storage, T_{sto} is ideally controlled at 25 °C.

The outlet molar flow is given by the valve equation

$$\dot{n}_{O_2}^{out} = k_{vlv} z \sqrt{p_{sto} - p_{out}}$$

3 Simulation and Results

This section discusses simulation of developed model for the hydrogen electrolyzer plant. First, the effect of power, coolant flow rate and outlet valve displacement on the system of identical electrolyzers is investigated to identify degrees of freedom available for stabilizing the controlled variables. Thereafter, the effect of parameters like faraday efficiency parameters (f_1 & f_2) and number of cells on individual electrolyzer performance is studied to justify that model simulation response is in accordance to the expected physical system behaviour.

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For dynamic simulations, steady state solution is used for initializing the problem. Circulating lye temperature at steady state is assumed to be 80 °C. Also, pressure drop of 1 bar is assumed across the outlet valve and outlet valve displacement, z is 0.4 for steady state calculation for valve constant k_{vlv} , such that

$$k_{vlv} = \frac{\dot{n}_{H_2}^{out} \text{ steady state}}{z} \quad 8$$

The volume of gas storages is 5 litres and outlet pressure of the gas leaving storage is taken to be 20 bars.

3.1 Effect of change in power and coolant flow rate on the electrolyzer

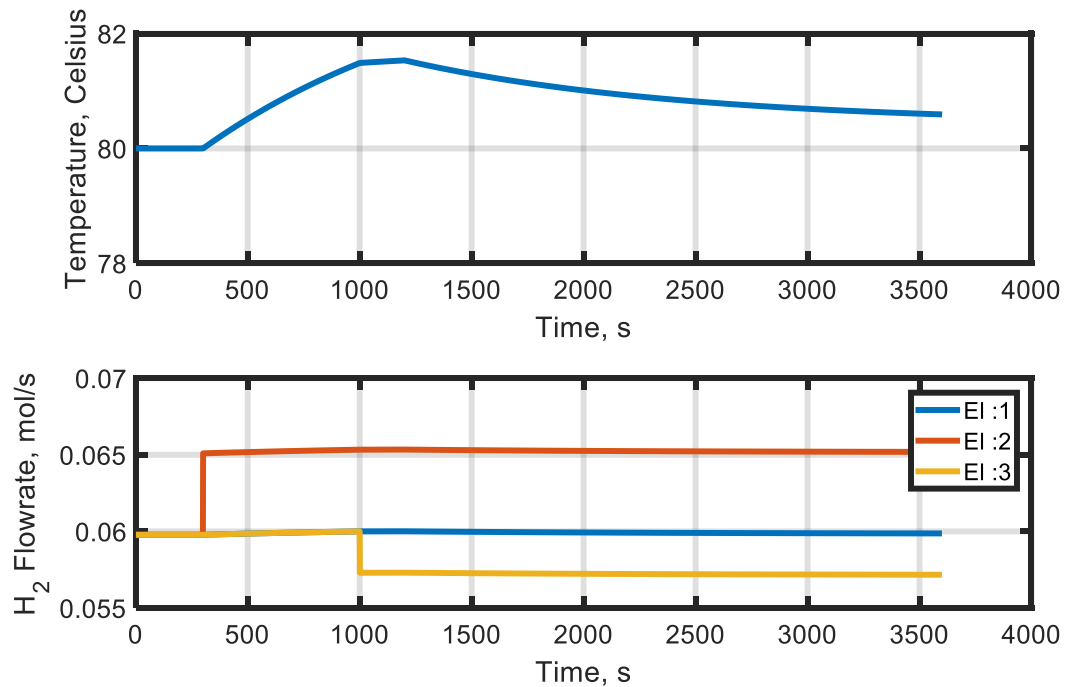


Figure 9: Effect of power and coolant flowrate on the electrolyzer system

Renewable power is intermittent in nature and therefore it is important to simulate the system for changing power input.

In this simulation, the model assumes that all electrolyzers have same values for faraday (f_1 & f_2), ohmic (r_1 & r_2) and overvoltage parameters (s , t_1 , t_2 & t_3). All 3 electrolyzers in electrolyzer stack are provided with same initial power of 21 kW at $t = 0$, and thereafter power to electrolyzer 2 is increased by 10% at $t = 300s$, whereas the power to electrolyzer 3 is reduced by 5% at $t = 1000s$. The temperature rise because of this intermittent power supply is stabilized by increasing coolant flow rate by 2.5% at $t = 1200s$.

As seen from the Figure 9, the increase in power to any one electrolyser increases the H_2 production from all other electrolyzers as well, in addition to significant increment of flow rate from the electrolyser which experiences change in power input. This can be explained by the fact that all the electrolyzers are coupled with each other because of

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the common lye temperature. Increment in power increases the temperature of the circulating lye which enhances the H_2 production from other electrolyzers. However, it is also important that temperature is controlled within certain range and this can be done by manipulating the coolant flow rate through the lye cooler. As we notice from the Figure 9, manipulating the coolant flowrate can reduce the temperature and thus will be an input for temperature control.

3.2 Effect of change in valve displacement on the storage

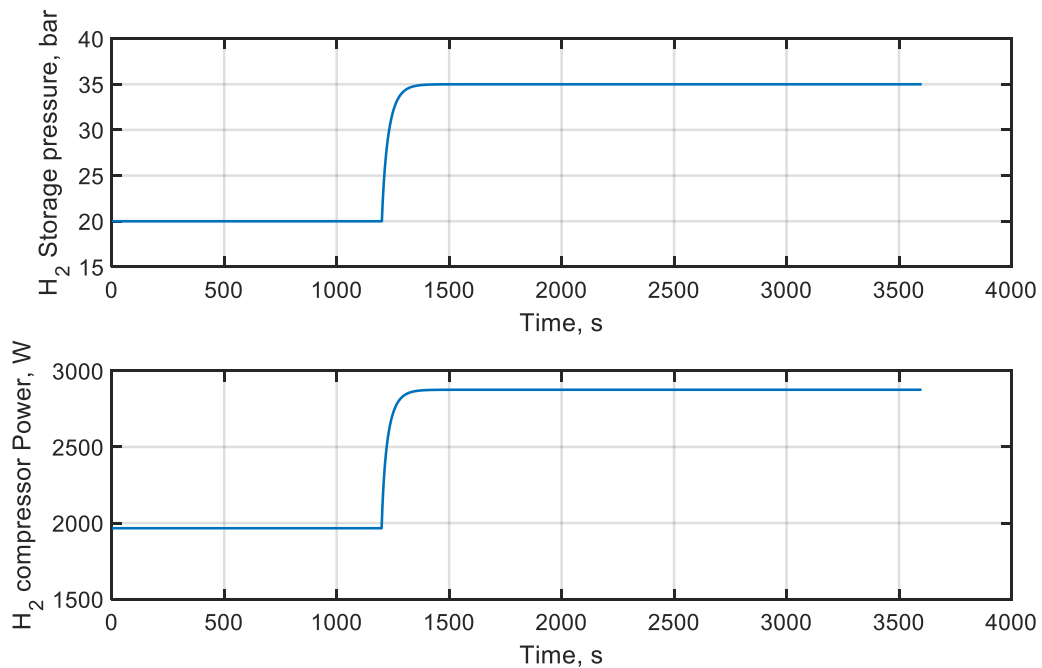


Figure 10: Variation in storage pressure and compressor power to the change in valve displacement

Like simulation in section 3.1, the model here also assumes that all electrolyzers have same values for faraday efficiency (f_1 & f_2), ohmic resistance (r_1 & r_2) and overvoltage parameters (s , t_1 , t_2 & t_3). All electrolyzers receive constant power supply of 21 kW each for the complete simulation time. However, the outlet valve displacement for H_2 storage is changed from its initial value of 0.4 at $t = 0$ to $z = 0.1$ at $t = 1200$ s.

As seen from the Figure 10, closing the outlet flow valve will increase the storage pressure. The increment in storage pressure will consequently require more compressor power to fill hydrogen in the storage tank.

These results also indicate that with the increase in H_2 production rate (because of increment in power input to the electrolyzer), more compressor power will be required to pump gas to the storage. Therefore, it will be interesting to study, how the fraction of compressor power to the total power changes with the intermittences in the renewable power.

3.3 Behavior of electrolyzers with different performance parameters

In this simulation, the response of electrolyzers with different values for performance parameters e.g. number of cells in electrolyzer and faraday efficiency parameter (f_1 & f_2) is discussed.

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3.3.1 Electrolyzers with different number of cells

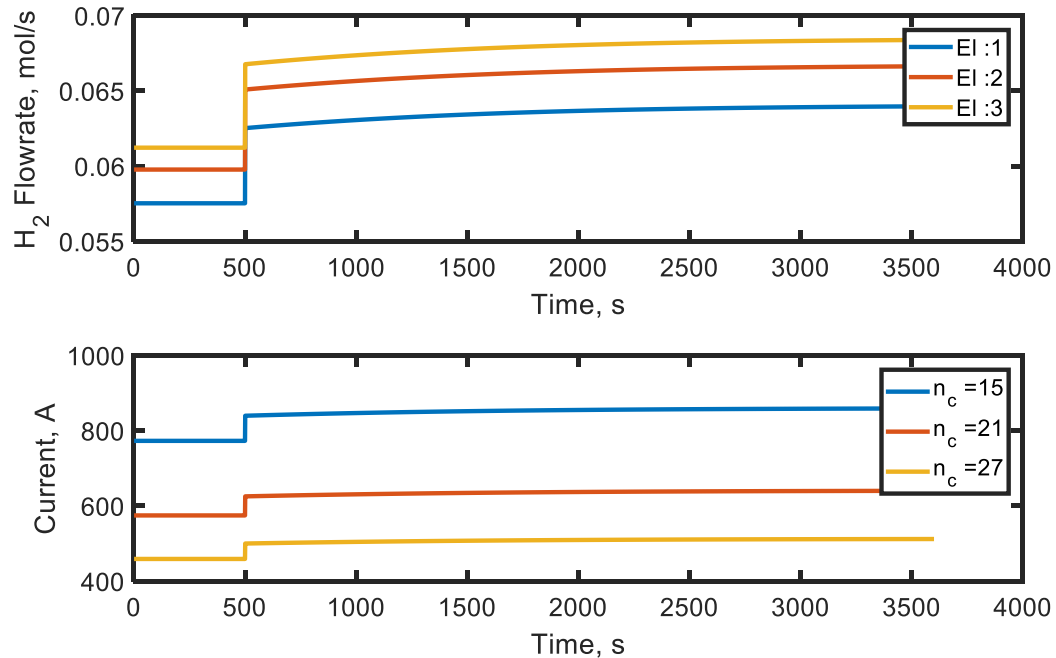


Figure 11: Performance of electrolyzers with different number of cells

Consider three electrolyzers with different number of cells, let each electrolyzer has 1,15 and 21 cells respectively. As we see in Figure 11, each electrolyzer has different performance characteristics. All the electrolyzers are provided with the same power of 21kW at $t = 0$, which is then increased by 10% at $t = 500s$.

Electrolyzer 1 has highest current flowing through each cell but as the number of cells is minimum, the total hydrogen flowrate through electrolyzer 1 is least. Therefore, it'd be safe to conclude that by increasing the number of cells and keeping power fixed, the total H₂ production will increase.

3.3.2 Electrolyzer with different values for faraday efficiency parameters

Consider different values of faraday efficiency parameter, f_1 in this simulation. All the electrolyzers are provided with the same power of 21kW at $t = 0$, which is then increased by 10% at $t = 500s$.

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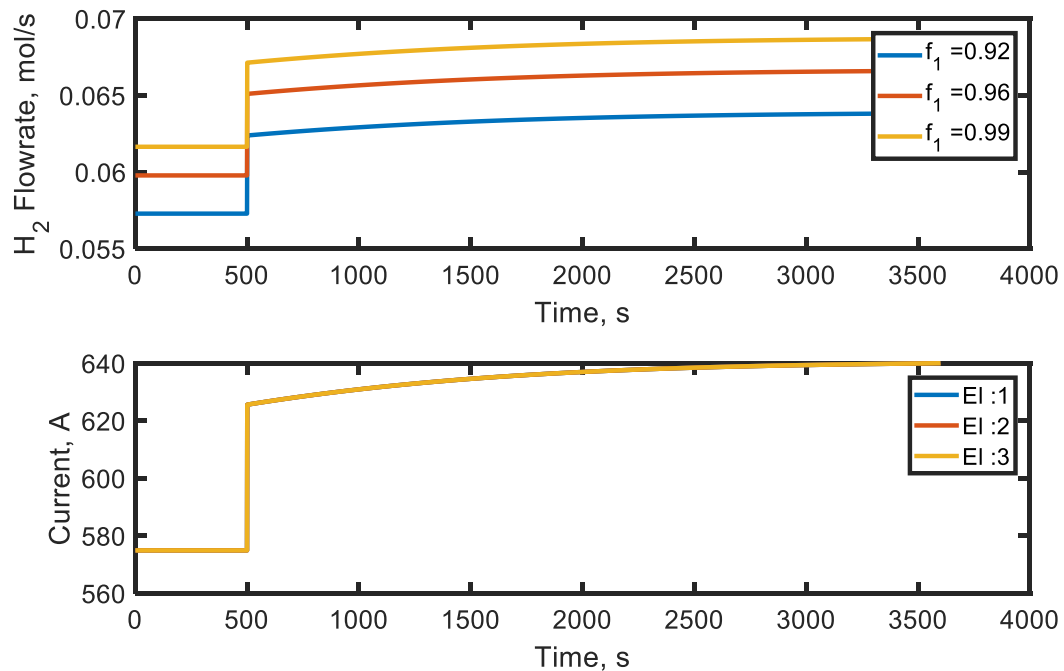


Figure 12: Performance of electrolyzer for different value of faraday efficiency parameter, f_1

It can be seen from Figure 12 that the faraday efficiency parameter only changes the net hydrogen flowrate from the electrolyzer and does not have any influence on the current flowing through each electrolyzer.

4

Conclusion and Recommendations

The model developed is used to simulate the simplified system of electrolyzers. The results of the simulation are in accordance to the Ulleberg's model results [4]. The simulation results for compressor and gas storage system also corroborate to our understanding of physical system behavior.

All the electrolyzers in this model has same temperature at inlet which is equal to the temperature of the incoming lye solution. This temperature is an important controlled variable as it decides energy efficiency of the electrolyzer. The temperature can be controlled using coolant flow rate, where the coolant flow rate through the cooler in lye circulation loop is considered as a manipulated variable in this model.

The developed model does not consider modeling of power electronics and assumes that the power for the operation of plant is obtained from renewable sources. The intermittences in the power can be handled by adjusting outlet flow rate from the storage tank. The model incorporates this system characteristic by using valve displacement as a manipulated variable.

4.1

Future work

Recommendation for further studies on the developed dynamic hydrogen electrolyzer plant model is summarized below:

The assumption that the temperature of all electrolyzers is same can be removed for the fact that material properties of each individual electrolyzer can be different which may

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lead to different thermal performances. Modifying current model to include this will need a separate heat balance per electrolyzer and an additional model for lye circulation system. Doing this will make electrolyzer model more realistic and will certainly improve the robustness of the dynamic model.

Ulleberg's model [4] for modeling I-U characteristics of electrolyzer is used in this model development. This is based on empirical correlations and depends only on temperature. The model robustness can be increased by using recently developed multi physics model [7] that considers variation of all structural and operational parameters (like material, temperature, pressure, concentration, bulk bubbling etc.) of the electrolyzer. However, it should be noted that involving these effects will undoubtedly increase the complexity of the model and there is a trade-off between the complexity and accuracy that needs to be decided.

The most challenging part with the use of renewable power is to handle the involved intermittencies. Therefore, designing a robust control structure is at the very core for successful implementation of this concept at plant scale. Control system design studies can be performed using this model. A comprehensive study on different possible control structures will help to identify manipulated variables and the controlled variables that needs to be stabilized.

During operation, the behavior of each individual electrolyzer in the system will be different after a certain time. The performance characteristics will be different for each electrolyzer. Therefore, power distribution to each electrolyzer needs to be optimized. This calls for the formulation of an optimization problem to maximize the total hydrogen production based on the individual electrolyzer performance and the total power.

5 List of Symbols

<i>SYMBOL</i>	<i>DESCRIPTION</i>	<i>UNIT</i>
A	Area of electrode	m^2
I	Current	A
emf	Electromotive force	V
U	Cell voltage	V
ΔG	Change in gibbs energy	$J mol^{-1}$
ΔH	Change in enthalpy	$J mol^{-1}$
ΔS	Change in entropy	$J K^{-1}mol^{-1}$
r_1	parameter related to ohmic resistance of electrolyte	Ωm^2
r_2	parameter related to ohmic resistance of electrolyte	$\Omega m^2 \text{ } ^\circ C^{-1}$
s	coefficient for overvoltage on electrodes	V
t_1	coefficient for overvoltage on electrodes	$A^{-1}m^2$

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t_2	coefficient for overvoltage on electrodes	$A^{-1}m^2\text{°C}$
t_3	coefficient for overvoltage on electrodes	$A^{-1}m^2\text{°C}^2$
η_F	Faraday efficiency	
η_e	Energy efficiency	
f_1	parameter related to Faraday efficiency	mA^2cm^{-4}
f_2	parameter related to Faraday efficiency	
\dot{n}	molar flow rate	mol/s
n_c	number of cells in series per stack	
C_t	overall thermal capacity of the electrolyzer	$J\ K^{-1}$
R_t	overall thermal resistance of electrolyzer	$W^{-1}\ K$
\dot{Q}	heat transfer rate	W
T	temperature	K or °C
τ_t	thermal time constant	s
k	Polytropic exponent	
γ	Adiabatic exponent	
α	Compressor efficiency	
w	Polytropic work	$J\ mol^{-1}$
E_p	Polytropic efficiency	
k_{vlv}	Valve constant	$mol/(s.\sqrt{bar})$
z	Valve displacement	

Subscripts

a	Ambient
$cool$	Cooling
$comp$	Compressor
gen	Generated
$loss$	Loss to ambient

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<i>sto</i>	Storage
<i>ini</i>	Initial
<i>rev</i>	Reversible
<i>tn</i>	Thermoneutral

Constants

<i>z</i>	Number of electrons transferred per reaction	2
<i>F</i>	Faraday constant	96485

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7 Appendix MATLAB Code

7.1 Main file

```
% Load CasADi
import casadi.*

%Using CasADi we are solving system of ODE and nonlinear algebraic eqns simultaneously
%1) UI*nc-Power = 0;
%2) U - (((r1+r2*T)*I)/A) - s*log10(((t1+(t2/T)+(t3/T^2))*I/A)+1) - Urev = 0;
%3) dT/dt = Qgen - Qloss - Qcool;
%4) Feff - ((.1*I/A)^2)/(f1+((.1*I/A)^2))*f2
%5) nH2 - Feff*nc*I/(ze*FC)
%6) nH2out - kvlvH2*VdispH2*sqrt(PstoH2-Pouth2)
%7) dPstoH2/dt = (TstoH2*Rg/VstoH2)*(nH2-nH2out)
%8) nO2out - kvlvO2*VdispO2*sqrt(PstoO2-PoutO2)
%9) dPstoO2/dt = (TstoO2*Rg/VstoO2)*(nO2-nO2out)
```

7.1.1 Loading parameters

```
global N
N = 3; %no. of electrolyzers
par = parElectrolyzer(N);

ze = par.Const.ze; %number of electrons transferred per reaction
FC = par.Const.FC; %faraday constant
```

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```
R = par.Const.R; %gas constant, [J mol^-1 K^-1,]
alpha = par.Comp.alpha; %compressor efficiency, 63%
k = par.Comp.k; %polytropic exponent, 1.62
Tel = par.Comp.Tel; %temperature of inlet to compressor after cooler, [Kelvin]
Pel = par.Comp.Pel; %pressure of electrolyzer outlet, [bar]
VstoH2 = par.Storage.VstoH2; %volume of H2 storage, litres
VstoO2 = par.Storage.VstoO2; %volume of O2 storage, litres
PoutH2 = par.Storage.PoutH2; %outlet H2 pressure, bar
PoutO2 = par.Storage.PoutO2; %outlet O2 pressure, bar
TstoH2 = par.Storage.TstoH2; %temp of H2 storage, kelvin
TstoO2 = par.Storage.TstoO2; %temp of H2 storage, kelvin
Rg = par.Storage.Rg; %gas constant in 1 bar K^-1 mol^-1
VdispH2 = par.Storage.VdispH2; %steady state valve displacement for hydrogen outlet
VdispO2 = par.Storage.VdispO2; %steady state valve displacement for oxygen outlet
```

7.1.2 Inputs for the simulation

```
Power = 21000; %net power to the plant, [Watts]
num_hr = 1; %no. of hours
t0 = 1; %start, [s]
ts = 1; %time step, [s]
tf = num_hr*60*60; %final, [s]
tsamp = t0:ts:tf;
len = length(tsamp); %number of simulation time steps
```

7.1.3 Steady state solution and calculation of valve constant

```
%The steady state solution is calculated independently for each individual
%electrolyzer and then used as initial state for solving the dynamic model

%Valve constant is calculated for steady state condition and is kept
%constant for rest of the simulation

T_ini = 80; %assumed steady state temperature

nH2ss = zeros(N,1); %H2 flow rate from electrolyzer at steady state, [mol/s]
nO2ss = zeros(N,1); %O2 flow rate from electrolyzer at steady state, [mol/s]
nH2sout = zeros(N,1); %H2 flow rate from storage at steady state, [mol/s]
nO2sout = zeros(N,1); %O2 flow rate from storage at steady state, [mol/s]
Qloss = zeros(N,1); %heat loss to ambient from electrolyzer, [Watts]
Qgen = zeros(N,1); %internal heat generation, [Watts]

z00 = zeros(1,6*N); %variable to store steady state solution of all electrolyzers
k_num=1; %counter for creating steady state solution vector of all electrolyzers

param = struct([]);
for j=1:N %sequence from 1 to N electrolyzer

    %parameter assignment
    nc = par.EL(j).nc;

    %initial guess for solving steady state
```



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end

```
% Calculation of valve constants
nH2ss = sum(nH2ss); %net hydrogen flowrate from all electrolyzers at steady
state(sum of individual contributions), [mol/s]
nO2ss = sum(nO2ss); %net oxygen flowrate from all electrolyzers at steady
state(sum of individual contributions), [mol/s]
nH2sout = sum(nH2sout); %net hydrogen flowrate from storage at steady state (sum of
individual contributions), [mol/s]
nO2sout = sum(nO2sout); %net oxygen flowrate from storage at steady state (sum of
individual contributions), [mol/s]
kvalveH2 = nH2ss/VdispH2; %valve constant for hydrogen outlet
kvalveO2 = nO2ss/VdispO2; %valve constant for oxygen outlet

Psto_iniH2 = (nH2ss/(kvalveH2*VdispH2))^2 + Pouth2; %initial H2 storage pressure
(calculated from steady state solution) [bar]/can be set manually
Psto_iniO2 = (nO2ss/(kvalveO2*VdispO2))^2 + PoutO2; %initial O2 storage pressure
(calculated from steady state solution) [bar]/can be set manually

x0 = [T_ini Psto_iniH2 Psto_iniO2]; %initial vector for dynamic solution
of differential variables
z0 = [z00 nH2ss nH2sout nO2ss nO2sout]; %initial vector for dynamic solution
of algebraic variables

%calculation of Qcool at steady state
Qgen = sum(Qgen); %rate of heat generation in the electrolyzer stack at steady
state
Qloss = sum(Qloss); %rate of heat loss in the electrolyzer stack at steady state
Qcool = Qgen-Qloss; %coolant flowrate at steady state
```

7.1.4 Manipulated variables

```
%these are the degree of freedoms that we will utilise to control the
%system

P = zeros(len,N); %power, [Watt], len is the length of time vector
for j=1:N
    P(1:500,j)=param(j).Pel*1; %incremental step change in power for all
electrolysers
    P(501:end,j)=param(j).Pel*1;
    %P(1001:end,j)=1.2*param(j).Pel;
    %P(1501:end,j)=0.8*param(j).Pel;
    %P(2001:end,j)=param(j).Pel*1;
end
% P(301:end,2)=param(2).Pel*1.1; %incremental step change in power for individual
electrolysers
% P(1001:end,3)=param(3).Pel*0.95;

Qc = Qcool*ones(len,1); %coolant flow rate as a manipulated variable
%Qc(1:500)=Qcool*1.2; %incremental step change in cooling rate
%Qc(501:end)=Qcool*1.5;
%Qc(1201:end)=1.025*Qcool;

ZH2 = VdispH2*ones(len,1); %H2 valve displacement as a manipulated variable
ZH2(1201:end) = .1; %change in H2 valve displacement

ZO2 = VdispO2*ones(len,1); %O2 valve displacement as a manipulated variable
%ZO2(501:end) = .7; %change in O2 valve displacement
```

7.1.5 Initialize plotting variables

```
Temp = zeros(len+1,1); %temp of the electrolyzer, [C]
Temp(1) = full(T_ini);

PstoH2 = zeros(len+1,1); %H2 storage pressure, [bar]
PstoH2(1) = full(Psto_iniH2);

PstoO2 = zeros(len+1,1); %O2 storage pressure, [bar]
PstoO2(1) = full(Psto_iniO2);

U = zeros(len,1); %voltage/cell in each of the electrolyzer, [V]
I = zeros(len,1); %current in each electrolyzer, [A]
I_den = zeros(len,1); %current density in the electrolyzer, [A/m^4]
nH2in = zeros(len,1); %net hydrogen flow rate in to the storage, [mol/s]
nH2out = zeros(len,1); %net hydrogen flowrate out from the storage, [mol/s]
nH2elout = zeros(len,1); %hydrogen flowrate from each of the individual
electrolyzer, [mol/s]
nO2in = zeros(len,1); %net oxygen flow rate in to the storage, [mol/s]
nO2out = zeros(len,1); %net oxygen flowrate out from the storage, [mol/s]
PcompH2 = zeros(len,1); %compressor power for hydrogen, [watts]
PcompO2 = zeros(len,1); %compressor power for oxygen, [watts]
```


7.1.6 Solving for T_{el},U,I,Feff,nH₂,nO₂

```
%T=x(1);PstoH2=x(2);PstoO2=x(3);
%U=z(6*j-5);I=z(6*j-4);Feff=z(6*j-3);nH2=z(6*j-2);Qgen=z(6*j-1);Qloss=z(6*j);nH2out=z(6*N+2);nO2=z(6*N+3);nO2out=z(6*N+4)

eqnAlg = SX.zeros(6*N+4,1);
eqnDiff = SX.zeros(3,1);
z = SX.sym('z',6*N+4); x = SX.sym('x',3); p = SX.sym('p',N+3);
%standard casadi notation, z: algebraic variable, x: differential variable,
%p: parameters (MV)

%here, we are now writing equations for transient behaviour of the electrolyzer.
for j=1:N

    %parameter assignment
    r1 = par.U(j).r1;
    r2 = par.U(j).r2;
    s = par.U(j).s;
    t1 = par.U(j).t1;
    t2 = par.U(j).t2;
    t3 = par.U(j).t3;
    f1 = par.U(j).f1;
    f2 = par.U(j).f2;

    Ct = par.TherMo(j).Ct;
    Rt = par.TherMo(j).Rt;

    Utn = par.EL(j).Utn;
    Urev = par.EL(j).Urev;
    nc = par.EL(j).nc;
    A = par.EL(j).A;
    Ta = par.EL(j).Ta;
    Tstd = par.EL(j).Tstd;

    %system of algebraic equations for an electrolyzer
    eqnAlg(6*j-5) = z(6*j-5)*z(6*j-4)*nc- p(j); %power = nc*UI
    eqnAlg(6*j-4) = z(6*j-5) - (r1+r2*x(1))*z(6*j-4)/A - s*log10(((t1+t2/x(1)+t3/x(1)^2)*z(6*j-4)/A)+1) - Urev; %U-I relationship
    eqnAlg(6*j-3) = z(6*j-3) - ((.1*z(6*j-4)/A)^2)/(f1+((.1*z(6*j-4)/A)^2))*f2;
    %faraday efficiency
    eqnAlg(6*j-2) = z(6*j-2) - z(6*j-3)*nc*z(6*j-4)/(ze*FC); %nH2 from individual electrolyzer
    eqnAlg(6*j-1) = z(6*j-1) - nc*(z(6*j-5)-Utn)*z(6*j-4); %Qgen eqn for individual electrolyzer
    eqnAlg(6*j) = z(6*j) - (x(1)-Ta)/Rt; %Qloss for individual electrolyzer

end

sum_H2net = SX.zeros(1,1);
Qgen_net = SX.zeros(1,1);
Qloss_net = SX.zeros(1,1);
```

Report

Knowledge grows

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Your Date
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```
for j=1:N
    sum_H2net = sum_H2net + z(6*j-2); %sum of hydrogen from all individual electrolyzers
    Qgen_net = Qgen_net + z(6*j-1); %total heat generated from all elctrolyzers
    Qloss_net = Qloss_net + z(6*j); %total heat loss from all electrolyzers
end

eqnAlg(6*N+1) = z(6*N+1) - sum_H2net; %algebraic eqn for net hydrogen
flowrate from all the electrolyzers
eqnAlg(6*N+2) = z(6*N+2) - kvalveH2*p(N+2)*sqrt(x(2)-PoutH2); %algebraic eqn for net hydrogen
flowrate from the storage tank
eqnAlg(6*N+3) = z(6*N+3) - z(6*N+1)/2; %algebraic eqn for net oxygen
flowrate from all the electrolyzers
eqnAlg(6*N+4) = z(6*N+4) - kvalveO2*p(N+3)*sqrt(x(3)-PoutO2); %algebraic eqn for net oxygen
flowrate from the storage tank

eqnDiff(1) = (Qgen_net - Qloss_net - p(N+1))/(Ct*N); %differential eqn for the lye
temperature
eqnDiff(2) = (TstoH2*Rg/VstoH2)*(z(6*N+1)-z(6*N+2)); %differential eqn for hydrogen
storage pressure
eqnDiff(3) = (TstoO2*Rg/VstoO2)*(z(6*N+3)-z(6*N+4)); %differential eqn for oxygen
storage pressure

dae = struct('x',x,'z',z,'p',p,'ode',eqnDiff,'alg',eqnAlg);
F = integrator('F','idas',dae);

for i=1:len
    %i = timestamp
    %j = electrolyzer sequence

    r = F('x0',x0,'z0',z0,'p',[P(i,:) Qc(i) ZH2(i) ZO2(i)]);
    x0 = full(r.xf); %updating solution as new initial conditions
    z0 = full(r.zf);
```

7.1.7 Storing values in plotting variables

```
%calculation of compressor power
PcompH2(i) = full(((r.zf(6*N+1)*k*R*Tel)/(alpha*(k-1)))*((r.xf(2)/Pel)^(k-1)/k)-1));
PcompO2(i) = full(((r.zf(6*N+3)*k*R*Tel)/(alpha*(k-1)))*((r.xf(3)/Pel)^(k-1)/k)-1));
%assuming same k and Tel for O2

Temp(i+1) = full(r.xf(1)); %temperature at all timestamps, [celsius]
PstoH2(i+1) = full(r.xf(2)); %hydrogen storage pressure at all timestamps, [bar]
PstoO2(i+1) = full(r.xf(3)); %oxygen storage pressure at all timestamps, [bar]
nH2in(i) = full(r.zf(6*N+1)); %net hydrogen flow rate in to the storage at all
timestamps, [mol/s]
nH2out(i) = full(r.zf(6*N+2)); %net hydrogen flowrate out from the storage at all
timestamps, [mol/s]
nO2in(i) = full(r.zf(6*N+3)); %net oxygen flow rate in to the storage at all
timestamps, [mol/s]
```

```
nO2out(i) = full(r.zf(6*N+4));           %net oxygen flowrate out from the storage at all
timestamps, [mol/s]

for j=1:N
    U(i,j) = full(r.zf(6*j-5));           %voltage/cell, [V]
    I(i,j) = full(r.zf(6*j-4));           %current, [A]
    I_den(i,j) = 0.1*I(i,j)/A;           %current density, [A/m^4]
    nH2elout(i,j) = full(r.zf(6*j-2));   %hydrogen flowrate from individual electrolyzer,
[mol/s]
end

disp(i)
end
```

7.1.8 Plotting the results

```
figure()
subplot(2,1,1)
plot(I)
xlabel('Time, s')
ylabel('Current, A')
legend(strcat('Electrolyzer ',num2str([1 2 3])))
subplot(2,1,2)
plot(U)
xlabel('Time, s')
ylabel('Voltage, V')
legend(strcat('Electrolyzer ',num2str([1 2 3])))

figure()
subplot(2,1,1)
plot(Temp)
xlabel('Time, s')
ylabel('Temperature, Celsius')
%ylim([78 82])
grid on
subplot(2,1,2)
plot(nH2elout)
xlabel('Time, s')
ylabel('H_2 Flowrate, mol/s')
legend(strcat('Electrolyzer ',num2str([1 2 3])))
grid on

figure()
subplot(2,1,1)
plot(PstoH2)
xlabel('Time, s')
ylabel('H_2 Storage pressure, bar')
ylim([15,40])
grid on
subplot(2,1,2)
plot(PcompH2)
xlabel('Time, s')
ylabel('H_2 compressor Power, W')
```



```
grid on
```

7.2 Steady state solution file

```
function [x0,z0] = elss(param,n)
%This function file solves the steady state solution for each of the
%individual electrolyzer
%Here we will assume steady state temp of lye as 80C

%n = sequence of the electrolyzer

%Here we are solving following eqns for each electrolyzer:
%1) UI*nc-Power = 0;
%2)  $U - ((r1+r2*T)*I)/A + s*\log_{10}(((t1+(t2/T)+(t3/T^2))*I/A)+1) - U_{rev} = 0;$ 

% Load CasADi
import casadi.*
global N
```

7.2.1 Load parameters

```
par = parElectrolyzer(N);

%parameter assignmemt
r1 = par.U(n).r1;
r2 = par.U(n).r2;
s = par.U(n).s;
t1 = par.U(n).t1;
t2 = par.U(n).t2;
t3 = par.U(n).t3;
f1 = par.U(n).f1;
f2 = par.U(n).f2;

Rt = par.TherMo(n).Rt;

Utn = par.EL(n).Utn;
Urev = par.EL(n).Urev;
nc = par.EL(n).nc;
A = par.EL(n).A;
Ta = par.EL(n).Ta;

ze = par.Const.ze; %number of electrons transferred per reaction
FC = par.Const.FC; %faraday constant
```

7.2.2 Define symbolic variables

```
x = SX.sym('x',2);
u=x(1);
i=x(2);
```

```
% Initial conditions for steady state calculations
Ps = param(n).Pel;           %initial guess for power, [watts]
u0 = param(n).u0;           %initial guess for voltage
i0 = param(n).i0;           %initial guess for current
T = param(n).T0;            %steady state temperature
% Ps = 4000;                 %initial guess for power, [watts]
% u0 = 1.3;                  %initial guess for voltage
% i0 = Ps/(nc*u0);           %initial guess for current
```

7.2.3 Solving steady state problem

```
g0 = u*i*nc-Ps;              % P=UI*nc, i.e. Power to
the electrolyzer, [Watts]
g1 = u - (r1+r2*T)*i/A - s*log10(((t1+t2/T+t3/(T^2))*i/A)+1) - Urev; %U-I relationship

g = Function('g',{x},{[g0;g1]});
G = rootfinder('G','newton',g);
res = G([u0;i0]);

U = res(1);
I = res(2);

% Residuals check
% eq1 = U*I*nc-Ps
% eq2 = U - (r1+r2*T)*I/A - s*log10(((t1+t2/T+t3/(T^2))*I/A)+1) - Urev
```

7.2.4 Calculation of initial state vector

```
Feff=((0.1*I/A)^2)/(f1+((0.1*I/A)^2))*f2;
nH2=Feff*nc*I/(ze*FC);

u_ini = U;
i_ini = I;
Feff_ini = Feff;
nH2el_ini = nH2;
nH2out_ini = nH2;
nO2 = nH2/2;
nO2el_ini = nO2;
nO2out_ini = nO2;

%Calculation of Qgen and Qloss at steady state assuming steady state temp to be 80C
Qgen = nc*(U-Utn)*I;         %heat generated in the jth electrolyzer
Qloss = (T-Ta)/Rt;           %heat loss in the jth electrolyzer

z0 = [u_ini, i_ini, Feff_ini, nH2el_ini, nH2out_ini, nO2el_ini, nO2out_ini];
x0 = [Qgen, Qloss];
end
```

7.3 Parameter file

```
function par = parElectrolyzer(N)
%This script defines values of the input parameters for all electrolyzers.

par.Const = struct('ze',2,'FC',96485,'R',8.314);
par.Comp = struct('alpha',0.63,'k',1.62,'Tel',25+273,'Pel',3);
par.Storage =
struct('VstoH2',5,'VstoO2',5,'PoutH2',19,'PoutO2',19,'TstoH2',25+273,'TstoO2',25+273,'Rg',8.314e-
2,'VdispH2',.4,'VdispO2',.4);
```

7.3.1 Parameters for U-I relationship in Ulleberg's model

```
par.U = struct([]);
par.TherMo = struct([]);
par.EL = struct([]);
for i =1:N
par.U(i).r1 = 8.05e-5;           %ohm m^2
par.U(i).r2 = -2.5e-7;          %ohm m^2 C^-1
par.U(i).s = .185;              %V
par.U(i).t1 = -.1002;           %A^-1 m^2
par.U(i).t2 = 8.424;             %A^-1 m^2 C^-1
par.U(i).t3 = 247.3;             %A^-1 m^2 C^-2
par.U(i).f1 = 250;               %mA^2 cm^-4
par.U(i).f2 = 0.96;              %dimensionless
```

7.3.2 Parameters for Ulleberg's thermal model

```
par.TherMo(i).Ccw = 0.7e3;           %thermal capacity of cooling water,
J s^-1 C^-1
par.TherMo(i).Ct = 625e2;           %625e3           %thermal capacity of electrolyzer,
J C^-1
par.TherMo(i).tauT = par.TherMo(i).Ccw*par.TherMo(i).Ct; %thermal time constant, Rt*Ct, [s]
par.TherMo(i).Rt = .167;             %C W^-1
par.TherMo(i).Tcwi = 14.5;           %inlet water temp, [C]
par.TherMo(i).hcond = 7;             %W C^-1
par.TherMo(i).hconv = 0.02;          %W C^-1 per A
```

7.3.3 Parameters for Faraday efficiency calculations

```
par.EL(i).Utn = 1.482;               %thermoneutral voltage, [V]
par.EL(i).Urev = 1.229;              %reversible cell voltage, [V]
par.EL(i).nc = 21;                   %no. of cells
par.EL(i).A = .25;                   %electrode area of each cell, [m^2]
par.EL(i).Ta = 20;                   %ambient temp, [C]
par.EL(i).Tstd = 25;                 %standard temperature, [C]
end
end
```