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21.1 Introduction

Design of high temperature PEM (HTPEM) fuel cell systems requires special consideration of the elevated temperatures, and proper heat integration. Due to the increased tolerance to impurities, such as CO, in the anode hydrogen fuel flow these systems have a high degree of flexibility when it comes to choice of fuel.

The shift towards higher temperatures is not without challenges, the materials (membranes, catalysts, stack and system components) are further stressed while also less mature, system start-up time is longer and performance is lower than Nafion-based systems. However, HTPEM fuel cell systems have the potential of obtaining comparable efficiencies with other fuel cell technologies and in some cases provide more advantageous solutions due to the ease of cooling, reduced requirements for fuel quality and the possibility of using more readily available fuels that require smaller investments in

infrastructure [1–4]. The introduction of fuel reformers also introduce additional complexity to a fuel cell system, and require in turn proper control strategies in order to obtain reliable and efficient system performance. This chapter presents some of the challenges and strategies involved with HTPEM fuel cell system design, some of the considerations to make, and examples of different relevant control strategies and their potentials for use in real operating systems.

21.2 Methanol Reformer Systems

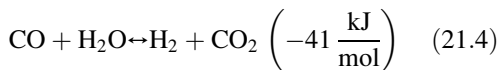
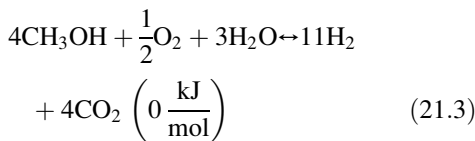
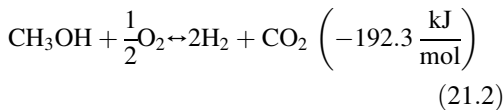
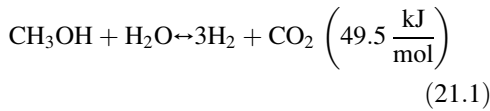
Using a liquid fuel, such as methanol, for fuelling a fuel cell system reduces or even eliminates some of the challenges involved with pure hydrogen-based fuel cells, such as the handling of non-conventional fuels, the distribution and availability, investments in infrastructure, and the low volumetric energy density, compared with liquid fuels even at high pressure (70 MPa). Methanol is the simplest alcohol, commonly used in the industry and therefore widely available. Although methanol mainly is produced from fossil natural gas, other, renewable onsite production methods are possible [5–9]. The temperatures of methanol steam reforming are low (220–300 °C) compared to the reforming of other commonly used fuels, such as natural gas or diesel (>700 °C). Low cost catalysts such as

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CuZn-based catalysts can be used, and different operating methods are possible. The most common reformer reactions can be seen in (21.1)–(21.4).



The most common efficient reforming method is the steam reforming reaction shown in (21.1), which is an endothermic reaction requiring addition of heat to the process. The other reactions ((21.2) and (21.3)) use an additional oxygen supply to the process, which in turn partially combusts some of the developed gasses. In the autothermal reforming reaction, (21.3), the heat generated by fuel oxidation is balanced to match the heat requirement for reforming. The resulting gasses of the steam reforming reaction are H_2 , CO_2 , H_2O , and CO and unconverted methanol fuel. It is of high importance to minimize the different pollutants in the hydrogen rich gas that enters the fuel cell stack, especially when it comes to CO and unconverted methanol, which will affect both the immediate stack performance and also lifetime [10–14]. Furthermore, the water-gas shift reaction (21.4) is an important process that typically occurs in parallel to the steam reforming reaction, converting part of the produced H_2 and CO_2 into CO and water forming a small amount of impurity in the fuel stream [15–18].

For methanol reformer systems to achieve optimal efficiencies proper heat integration is needed, i.e., all practically usable waste heat should be utilized. Different major heat consumers exist in HTPEM fuel cell systems,

such as fuel-water mixture evaporation and superheating as well as reformer reaction heat requirements. The main heat sources considered in the following shown cases are the fuel cell stack cathode exhaust and the unused anode exhaust gasses. Different system configurations are possible for transferring heat from and to these sources; the following examples will present a system topology using air and combusted gasses as the main heat carrier for transferring heat in the system. Mainly heat from the fuel cell stack is used to facilitate the evaporation of the methanol/water mixture entering the reformer. An alternative system is presented that uses a heat transfer oil as medium for transferring heat in the system using two different cooling circuit topologies.

21.3 Air Cooled Systems

Previous work has presented the use of air and as the heat transfer medium in HTPEM fuel cell stacks, this can be either as stacks with separate cooling channels or as cathode air cooled stacks, where cathode air at very high stoichiometry is used for controlling the temperature of a fuel cell stack [19]. This often yields very simple systems because fewer Balance-of-Plant components are needed and stack design often is simpler [20]. Careful flow field design is required in order to ensure low pressure drops in manifolds and cathode air flow fields. Both are required in order to use low power consuming air supplies, such as blowers and fans, and still ensure minimal parasitic losses in the system. Obtaining a uniform cell temperature is another challenge, ensuring a low temperature difference, not only within the individual MEAs from outlet to inlet, but also within the fuel cell stack. In the case where a methanol reformer system is introduced, the waste heat from the fuel cell cathode can effectively be used as process heat for evaporating the methanol/water mixture used in the reformer system. Figure 21.1 shows a schematic of a reformed methanol HTPEM fuel cell system using air-based cooling and heat transfer.

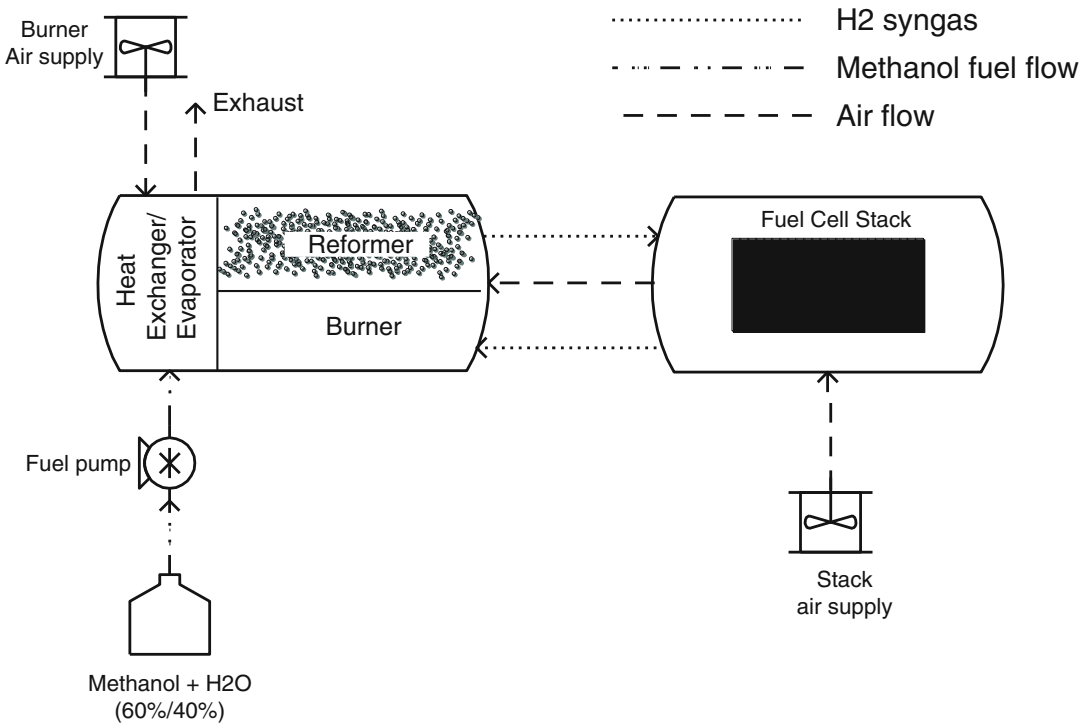


Fig. 21.1 Reformer system using air and flue gasses for heat transfer

The heat required by the methanol reforming process, which normally takes place at temperatures higher than the 160–180 °C of the fuel cell stack, can be supplied from the combustion of excess hydrogen exiting the fuel cell stack anode. An excess amount of hydrogen is normally supplied to the fuel cell stack, i.e., the fuel cell stack is running at a stoichiometry of $\lambda_{(H_2)} = 1.1–1.4$ in order to avoid dilution effects and ensure proper performance, because of the presence of residual gasses such as CO₂, CO, H₂O, and unconverted CH₃OH. This anode waste gas is catalytically combusted in a burner, and the heat is used to keep the reformer active at the desired operating temperatures (280–300 °C). Air is supplied to the anode waste gas, and provides the oxidant for the combustion process. The burner air flow is adjusted to control the resulting flue gas temperature, which is sent across a network of heat exchangers that preheat incoming gasses and supplies the catalyst bed with heat. Several authors have examined reformers using different types of system



Fig. 21.2 Commercial HTPeM reformed methanol fuel cell system (Serenergy H3-350) [25]

integration approaches [21–24]. An example of a commercial HTPeM fuel cell system as the one exemplified above is the Serenergy H3-350, which uses a similar operating principle as

shown in Fig. 21.1. The system can be seen in Fig. 21.2, and is usable as an off grid battery charger, as it has a DC/DC controlled power output able to charge, for example, a battery pack.

The system includes the integrated fuel cell stack and methanol reformer system, DC/DC converter and Balance-of-Plant components and a small fuel buffer tank. The system requires connection to a battery pack and a fuel tank dimensioned to the desired run-time of the system. Generally start-up is one of the main challenges with high temperature PEM systems and reformers also add additional components that require heating. System components such as stacks and reformers can often be heated by electrical heating elements because of the low mass and fast temperature transients, but in order to increase the system round trip efficiency, decrease initial required battery capacity, and reduce required battery pack load in the initial stage of system start-up, it is also possible to use the available methanol fuel for system preheating, as discussed later in “Methanol combustion heating.”

21.4 Liquid Cooled Systems

When increasing power levels, losses are also increased, and in order to keep system size

compact, efficiency high and ease connections to utilize waste heat, liquid-based heat transfer is often advantageous. Several authors have examined such cooling strategies for high temperature PEM fuel cell stacks [26–31]. Using a liquid cooling media of course requires additional cooling channels in the fuel cell stack assembly, and in many cases a high degree of engineering in order to properly chose gaskets and materials that are able to handle the high temperatures and offer stability over the entire lifetime of the fuel cell system. Furthermore, additional system components are needed in order to exchange heat between different temperature levels, and properly cool the different components; different heat exchangers and coolers are in this case needed. With circulating liquids, flows can be increased efficiently compared to increasing the flow from air compressors and fans that have larger energy consumption. Hence, more uniform temperature profiles can be expected on both reformer and fuel cell stack compared to systems using air cooling. Amongst others, Dudfield et al. [31] present an example of a reformer system using a thermal oil.

An example of a prototype reformer design for a liquid thermal oil system is presented in Fig. 21.3. In this case the reformer is designed as a cylindrical reactor with internal pipes containing catalyst material resembling a shell-and-tube heat exchanger. The methanol fuel

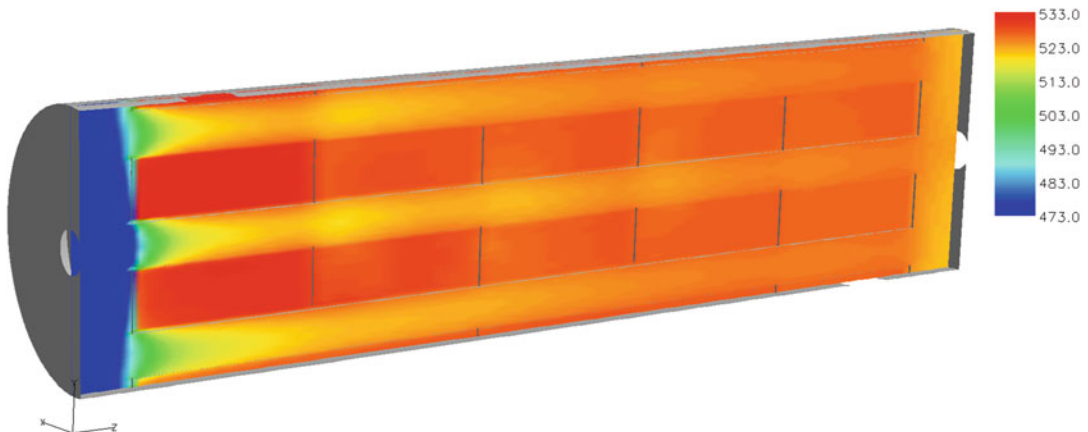


Fig. 21.3 Oil heated methanol reformer for 5 kW HTPEM fuel cell system. Temperature in the reactor center plane. Oil inlet temperature: 533 K. Methanol water mixture inlet temperature: 473 K

mixture flows in the tubes and thermal oil on the shell side provides heat for the reforming reactions. Figure 21.3 shows a cross section of the reactor temperature distribution in the center plane based on a detailed computational fluid dynamics analysis. The left cold part of the reformer is the fuel inlet manifold, not surrounded by the thermal oil, therefore at a lower temperature than the reformer itself. Simulations such as this are important tools in identifying possible shortcomings of reformer designs and identification of possible features that could benefit system design and control. Reformer reactor designs and operation conditions can be studied in detailed before the reactor is manufactured leading to significantly faster product development.

One desired feature to introduce to system control could be the possibility of changing output gas composition by shaping the temperature

profile of the reactor. The output gas composition is highly dependent on temperature and proper knowledge of reformer behavior could enable more intelligent control of the entire system to possibly decrease CO concentration in different system operating states or during transients, and hereby optimize performance and lifetime of the systems.

There are several system heat integration topologies using thermal oils such as Duratherm [32], Paratherm [33], and similar as heat transfer fluid. Two examples will be shown here, a parallel and serial topology. First, an example of a parallel system configuration is shown in Fig. 21.4.

The parallel system configuration shows two thermal oil subsystems, a low temperature (160–180 °C) and a high temperature (300 °C) subsystem. The low temperature subsystem includes the fuel cell stack, the evaporator for

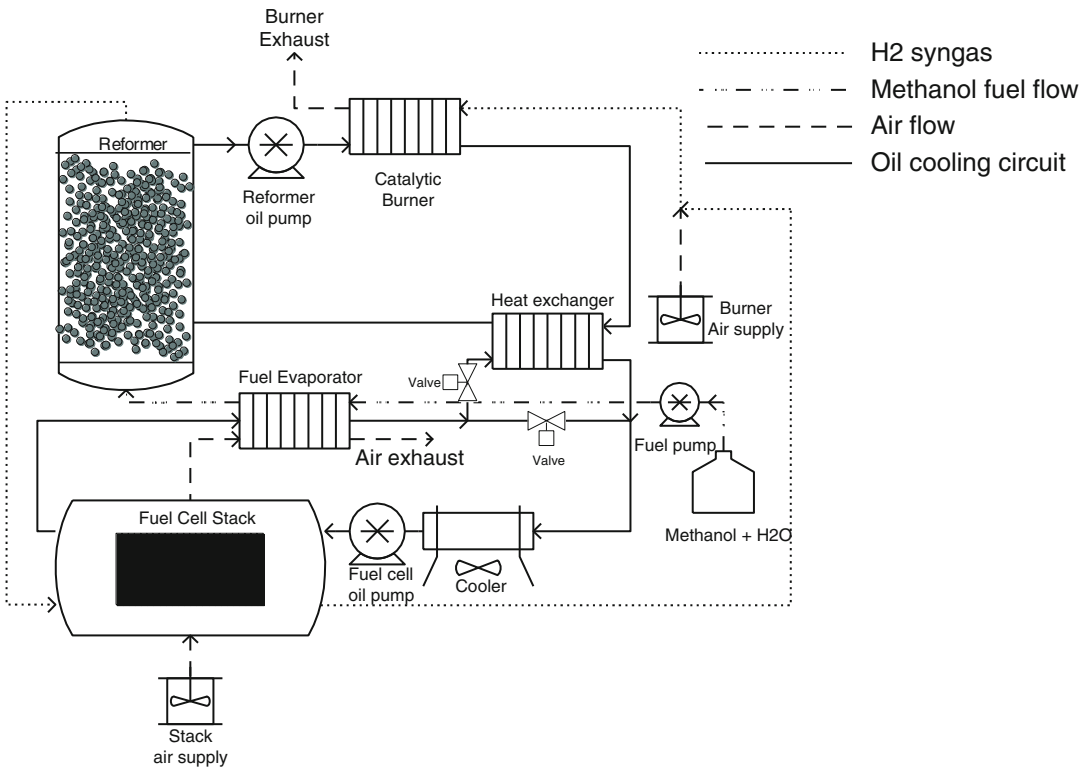


Fig. 21.4 Parallel thermal network example, liquid heat transfer using thermal oil. Two thermal subsystems, one with high temperatures (280–300 °C) including the

reformer and one with low temperatures including the fuel cell stack (160–180 °C)

the fuel water mixture, and a convective cooler with a fan. In the presented case, the evaporator receives heat from the cathode exhaust and the fuel burner. The high temperature subsystem includes the methanol reformer, a heat exchanger for extracting excess heat from the fuel burner, which runs of the unused fuel exiting the fuel cell stack anode. In start-up mode, the fuel burner runs of the methanol/water mixture assisted by a few electrical heaters for the initial start of the burner in case of low temperatures. The heat generated is transferred to the two subsystems, and preheats the fuel cell stack and the reformer before the systems are ready to deliver power. With individual pumps in each oil circuit, efficiency can be maximized by adjusting pump flow according to the particular state that the system is in or adjusting it according to the load on the system. One of the challenges when using reformer systems is during reductions in the load on the fuel cell stack. In such cases, fuel delivery must closely follow the reduction in power delivery from the fuel cell stack; otherwise the burner can experience a sudden temperature increase due to the increase in residual

hydrogen in the anode exhaust leading to a sudden increase in the heating value of the gas entering the burner. Such sudden changes could result in failure of the burner and possible meltdown due to extreme temperatures. For this reason a cooler is mounted to enable the possibility of reducing too high inlet temperatures during thermal transients, and for safe shut down of the system. Because the burner is the main source of heat, this is also the active part when starting up the system. The most efficient way of heating the system would be to combust fuel during start-up. As the oil in the high temperature circuit heats, the low temperature oil circuit can be bypassed through a heat exchanger for preheating the fuel cell stack. Start-up time of fuel cell stacks is a continuous focus point of high temperature fuel cell systems [34–38].

In order to simplify system design a serial thermal connection can be designed using a single pump, and an oil subsystem with several temperature levels. An example of such a system design is presented in Fig. 21.5.

The oil flow exiting the fuel burner represents the highest temperature, cooling the oil slightly

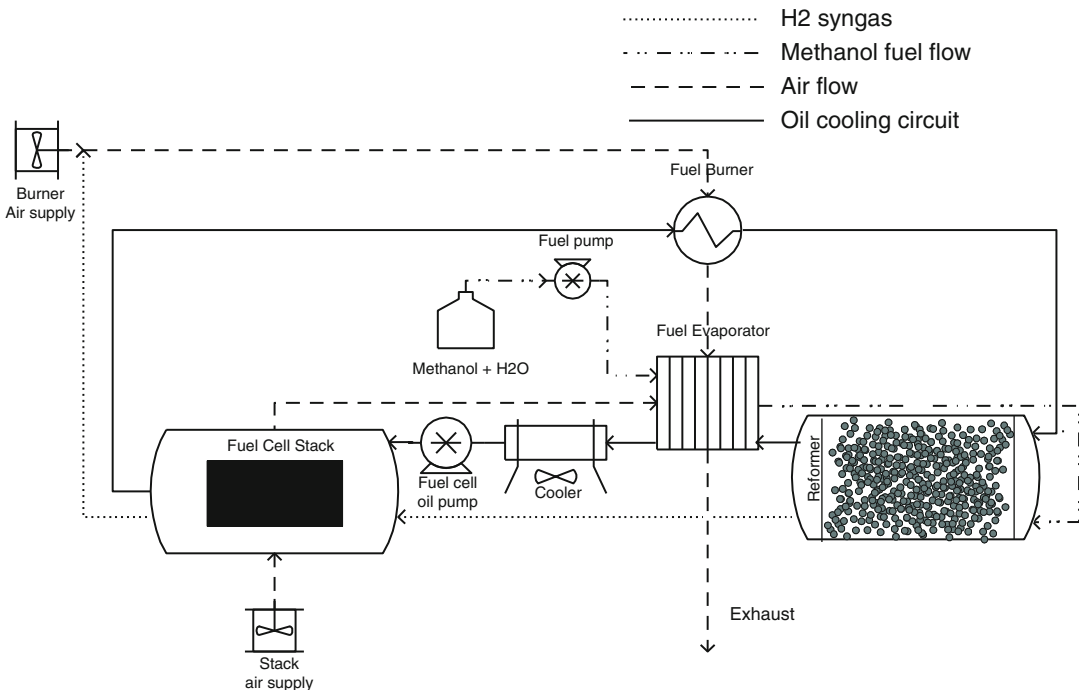


Fig. 21.5 Serial thermal network example, liquid heat transfer using thermal oil

as it transfers heat to the reformer. The main cooling under normal operation is in the fuel evaporator, where the oil needs to be cooled to around stack temperature. In case of temperature transients and critically high temperatures a cooler can be inserted enabling more control of the oil temperature. During start-up the fuel burner will initially be heated by a small amount of electrical energy, once switching to the combustion of the methanol fuel mixture, the components in the system will gradually heat. Thermal management of such a system is complex, and many of the components are able to affect the oil temperature. The components that can be directly controlled are the fuel burner, where air supply can be used to control temperature, the cooler, where an air fan can adjust the heat removal, and the fuel pump, which can change temperature profiles throughout the system.

Other thermal topologies within each of the proposed cases are also possible, and in case of further use for heat, heat exchangers can easily be added. Other more exotic cooling strategies are examined [39–41], but the objectives still remain, good temperature distribution, low parasitic losses, and good heat transfer.

21.5 Hydrogen vs. Reformer Systems

Pure hydrogen-based, and reformer-based systems have each their advantages and disadvantages. Hydrogen systems offer high electrical stack efficiencies, due to the absence of impurities and diluents, show the simplest system design, with low components count, and low parasitic losses. They have the possibility of dead-end operation because build-up of excess water is not an issue as it sometimes is in Nafion-based systems. The reformer-based systems on the other hand have the possibility of a higher degree of fuel flexibility, but at the cost of higher system complexity, introducing more components, and increasing the importance of predicting gas composition and stack performance. Dependence on CO concentration and

the dilution effect of CO₂ can induce significant changes in performance. Figure 21.6 shows a series of polarization curves of a single cell BASF PBI MEA, where various concentrations of CO and CO₂ in hydrogen is examined. Performance clearly diminishes with increasing CO concentrations, and the dilution effects of CO₂ are also visible.

The plot shows the immediate effects of CO over a few hours of operation, other than affecting this immediate performance, CO also has effects of the degradation of the MEA particularly at high concentrations. Modifications to the MEAs can often improve the performance of the increased degradation when running with impurities and higher temperatures [42]. Besides the immediate effects of CO poisoning visible on the polarization curve, the AC impedance is also affected. Figure 21.7 shows the impedance of single cell performance under different syngas compositions.

This effectively means that variations in gas composition affect not only the steady-state performance of the fuel cell, but also the transient electrical characteristics. Upon closer analysis it is clear that CO primarily changes the low frequency behavior of the fuel cell, resulting in a more sluggish electrical behavior at high CO concentrations. In order to compensate for the decreased voltage performance of the fuel cells when running with CO in the anode, the stack temperature can be elevated, which effectively increases the rate of CO kinetics and regains parts of the lost performance however at the expense of increased degradation by other mechanisms. Figure 21.8 shows polarization curves based on the semi-empirical model of Korsgaard et al. [43], comparing the performance between operation at 160 and 180 °C at different CO concentrations.

In order to show the significant influence, CO concentrations up to 50,000 ppm are shown. Increasing temperatures by 20 °C significantly improves the performance of the fuel cell.

Not only CO and CO₂ cause performance changes when using reformer systems, the exact influence from the presence of increased water content and possible membrane hydration is not

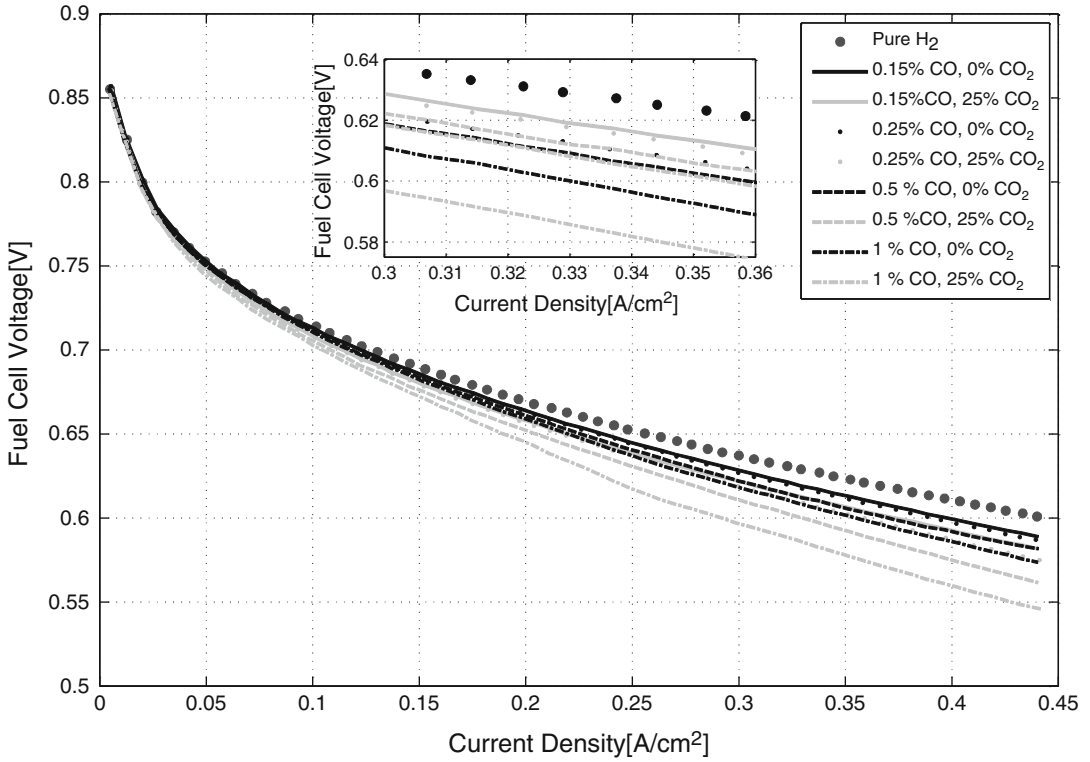


Fig. 21.6 Polarization curve on a 45 cm² single cell at 160 °C with different gas concentrations. Reproduced from [13] with permission Elsevier

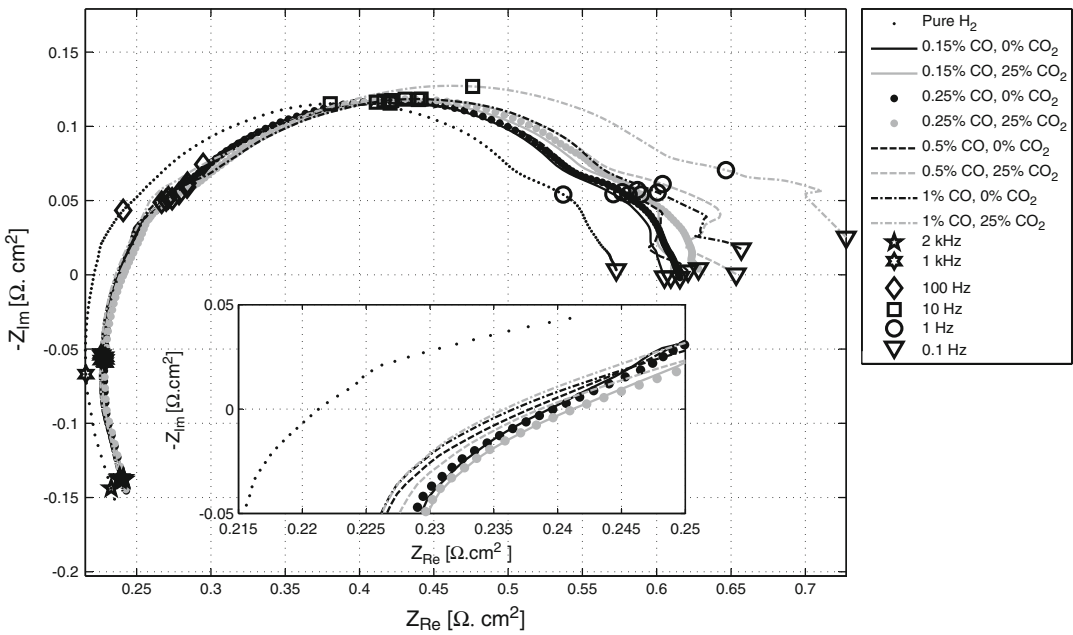


Fig. 21.7 Impedance plot of single cell performance on different syngas concentrations at 160 °C. Reproduced from [13] with permission of Elsevier

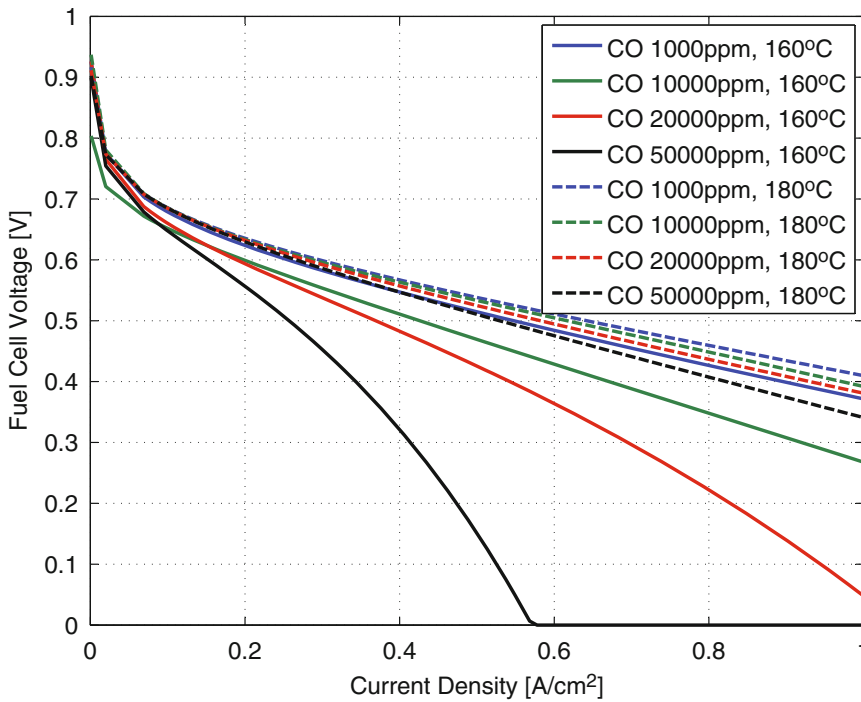


Fig. 21.8 Polarization curve of BASF HTPEM Celtec MEA at different temperatures and different CO concentrations [44]

fully understood. Several authors have examined the topic in recent studies [45–49]. Furthermore the effect of accumulated water in a system can affect the start-up time due to the additional requirement of water evaporation before start-up temperatures can be achieved.

Systems using HTPEM fuel cells and methanol reformers offer a solution where the electrical efficiency often is smaller than that of pure hydrogen-based HTPEM fuel cell systems, but there are still possibilities of improving many different aspects of these technologies, to increase performance, and the potentials could be to improve the total system efficiency beyond that of the pure hydrogen-based HTPEM systems. A large amount of heat is needed to evaporate the water/fuel mixture, which is often running at steam-to-carbon ratios of down to 1.5. Further increases in system efficiency could be achieved by lowering the amount of water and hereby the needed for additional energy for evaporation. Figure 21.9 explores the potential by comparing an ideal reformer system where

reforming temperature corresponds to the stack temperature, the steam-to-carbon ratio is 1, and no CO is present in the produced hydrogen. In such a case the waste heat is not only usable to evaporate the water/fuel mixture, but could potentially also be used as heat input to the reformer.

Such low temperature methods and catalysts are examined and show promising results [50–54]. Further details analyzing Balance-of-Plant power consumption of such system is needed as well as a thorough understanding of the feasibility from an engineering point of view is needed in order to evaluate the true potential of such a solution however it still indicates the potential of such systems.

21.6 Control of HTPEM FC Systems

In order to fully utilize the benefits of fuel cell systems and the power they deliver, and ensure stable reliable operation, proper control during

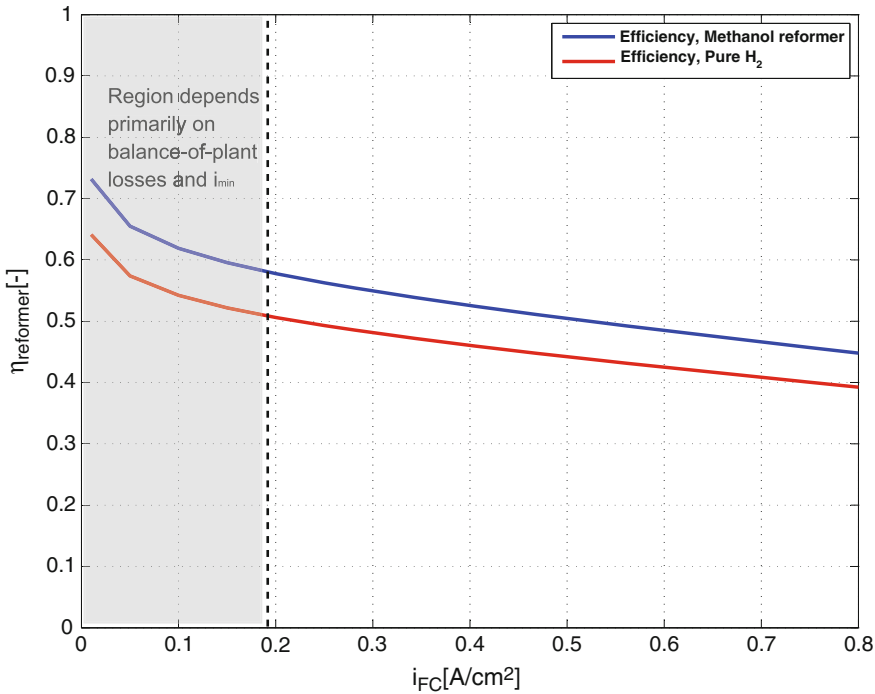


Fig. 21.9 System efficiency of fuel cell stack reforming at stack temperature and running on pure hydrogen, respectively [44]

the different operating regimes and lifetime of the fuel cell systems is critical. Fuel cell systems are highly nonlinear and complex and therefore often a challenging control task, especially if adaptability to changing ambient conditions and varying load profiles are of importance. The different operating regimes of fuel cell systems include:

- System start-up
- Power delivery
- System shutdown

In each of such operating regimes control plays an important part for ensuring long lifetime, safe operation, and optimized performance. In the following sections each of these regimes will be addressed, and examples of critical issues to address will be brought forth.

21.6.1 System Start-Up State

High Temperature PEM fuel cells use the proton conducting capabilities of phosphoric acid in order to conduct protons, as opposed to water-based PEM FCs, this allows operation above 100 °C with the increased boiling point of phosphoric acid. Although the increased temperatures offer faster kinetics and a much higher tolerance to pollutants, there is still a risk of acid leaching due to various mechanisms, one of which could occur during start-up of these systems if, for example, liquid water is produced. For this reason it is often important to preheat HTPEM FCs before drawing current [34, 36, 55]. This is in any case needed because fuel cells perform poorly at low temperatures. Figure 21.10 shows a comparison of the performance of a 45 cm² BASF Celtec-P MEA on pure hydrogen at different temperatures.

In the shown example a difference in voltage of 100 mV at the same current but different

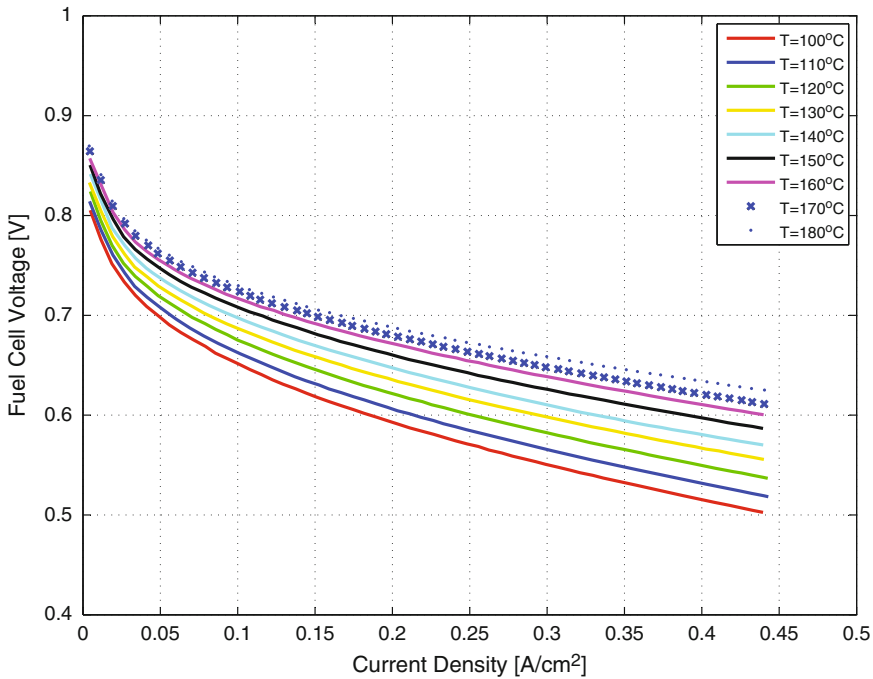


Fig. 21.10 Polarization curve using pure hydrogen at different temperatures [56]

temperatures can be observed, which is one of the reasons why reaching the correct temperatures before drawing high currents is important. Little knowledge of low temperature operations impact on lifetime exists. Although tendencies indicate that lower temperatures in the range of 140–150 °C increases lifetime, no one has examined how temperature below that will affect lifetime. Low temperature operating capabilities differ between MEA types and is an area only a few authors have explored.

21.6.1.1 Electrical Heating

Preheating of fuel cell stacks can be done in many ways, often the challenge is not only ensuring a certain temperature above 100 °C before drawing a current, but optimizing start-up speed and avoiding potentially harmful temperature overshoots while heating is also important. Figure 21.11 shows, for a particular system, how electrical input power affects fuel cell stack heating time.

Of course the challenge is not only achieving fast enough heating time, but just as much ensuring efficient heat. The use of direct electrical heating is often not a good idea, when also accounting for the additional power production need for recovering this used electricity and ensuring the availability of it in a system upon shutdown, such that the next start-up of the system is also possible.

21.6.1.2 Methanol Combustion Heating

The power required for preheating is also of significant importance. The energy used to heat a system should always be taken into account when calculating the efficiency and energy use of a fuel cell system. This means that the use of electrical heating often leads to a poor round-trip efficiency because the fuel cell system needs to produce the energy spent during preheating before a net power production is achieved. Furthermore electrical systems must take into account the extra electrical energy storage needed for enabling start-up which is both costly,

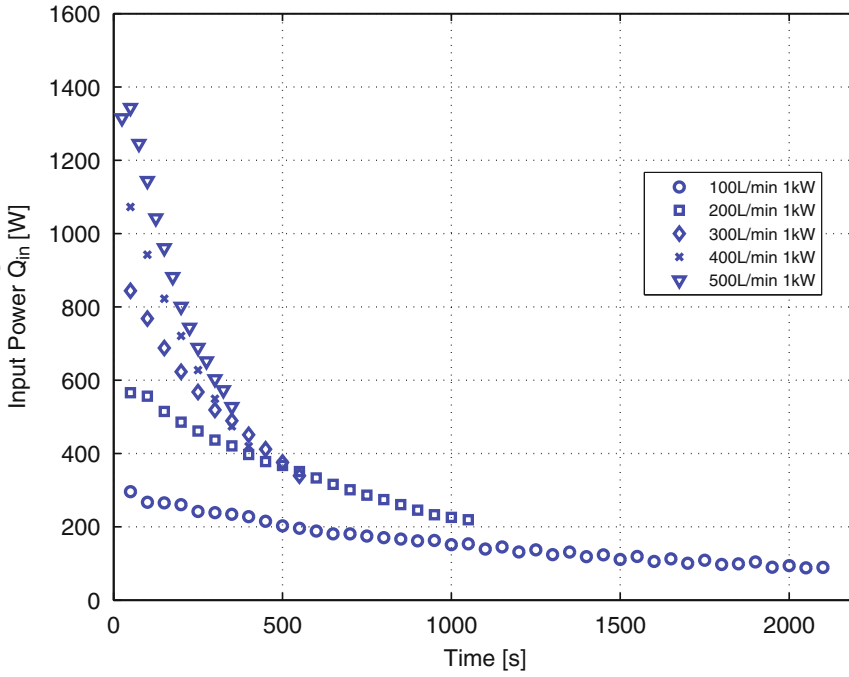


Fig. 21.11 Input power as a function of heating time at different cathode air flows at electrically preheated 1 kW cathode air cooled fuel cell stack. Reproduced from [34] with permission of Elsevier

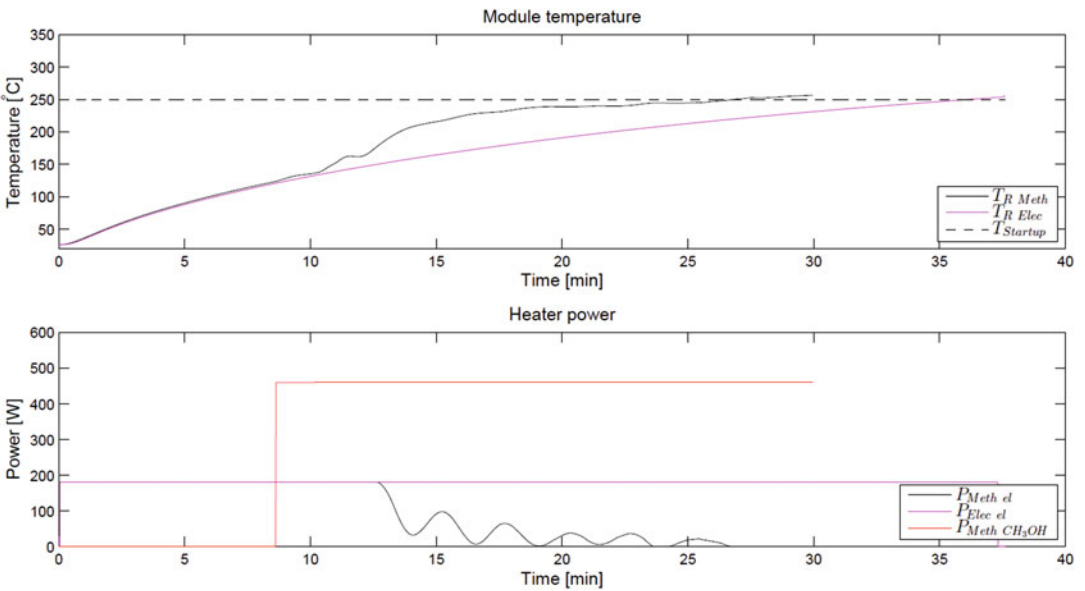


Fig. 21.12 Temperature development during heating of methanol reformer for H3-350 HTPEM FC system with and without methanol combustion

and often puts a significant additional load on a battery system during start-up because it not only needs to handle power consumption of the given application, but also the power requirements for starting up the fuel cell system. Figure 21.12 shows an example of the temperature development of a methanol reformer with an integrated burner for more efficient system start-up. In the shown example, T_{R_Meth} in the top plot is the temperature development in the reformer when a methanol/water mixture, with a steam-to-carbon ratio of 1.5, is added during start-up and T_{R_Elec} is the temperature development when pure electrical heating is used. The bottom plot shows the power added to the burner during the experiments. P_{Meth_el} is the electric power added during the experiment and $P_{Meth_CH_3OH}$ is the power added to the burner in the form of methanol during the same experiment. P_{Elec_el} is the electrical heating power during the pure electric experiment. Fuel with this steam-to-carbon ratio is used because it is available in the system already, eliminating the need for an extra tank.

From the figure it can be seen that the reformer reaches an operating point of 250 °C 10 min faster and at the cost of less electrical energy using methanol in the burner. The total energy consumption of a start-up is, however, larger during a methanol start-up due to the heating and evaporation of the water in the fuel and the heating of the burner's process air flow. But as the reduction in electric energy consumption means that the module achieves positive energy production more rapidly and increases the roundtrip efficiency, it is still considered a good idea.

The shown start-up example did not include an optimization or exploration of optimizing the start-up time. But several parameters can be adjusted to affect the dynamic characteristics of the initial preheating process of the reformer in question: fuel flow, air-to-fuel ratio, oxidant supply control, and steam-to-carbon ratio.

Start-up of an entire fuel cell reformer system could also be divided into different phases in order to decrease start-up time, by, for example,

starting to deliver a small amount of fuel cell stack power at 80 °C. This will often decrease heating time because the power production and losses, which are occurring on the MEAs themselves, are often more efficient than indirect heating by external heating elements, liquid heat transfer, or similar.

21.6.2 Power Delivery State

Upon proper system heating, and introduction of anode and cathode species, the fuel cell voltage will start rising to open circuit potential, and power can be drawn from the system. OCV operation of HTPEM fuel cells involves high potentials and as carbon corrosion is severely increased at high temperatures a certain amount of load is therefore recommendable to avoid these increased losses. One strategy is to use an external dump load, and waste the electrical energy, but a better option is to dissipate the energy in the systems electric heaters to keep the system heated. One of the challenges of operating at low power for systems like this is the required heat to keep the system at full operating temperature. Another solution could be to use part of the fuel cell power to supply power for the balance of plant, keeping system components powered. In any case both would be required in order to avoid prolonged exposure to the high potentials of OCV operation or possibly the need to shut down due to the system not being able to sustain the temperatures required for operation. Typically the regimes of operation can be defined, as the example shown in Fig. 21.13.

At low currents the fuel cell stack is typically very efficient, but at too high efficiencies stack temperature can drop and lower performance and eventually require system shutdown. In the same region of operation, there will be a point at which the fuel cell system components, the Balance-of-Plant, are using more power than the system is actually producing, at some point it would be a better solution to shut down the system and wait

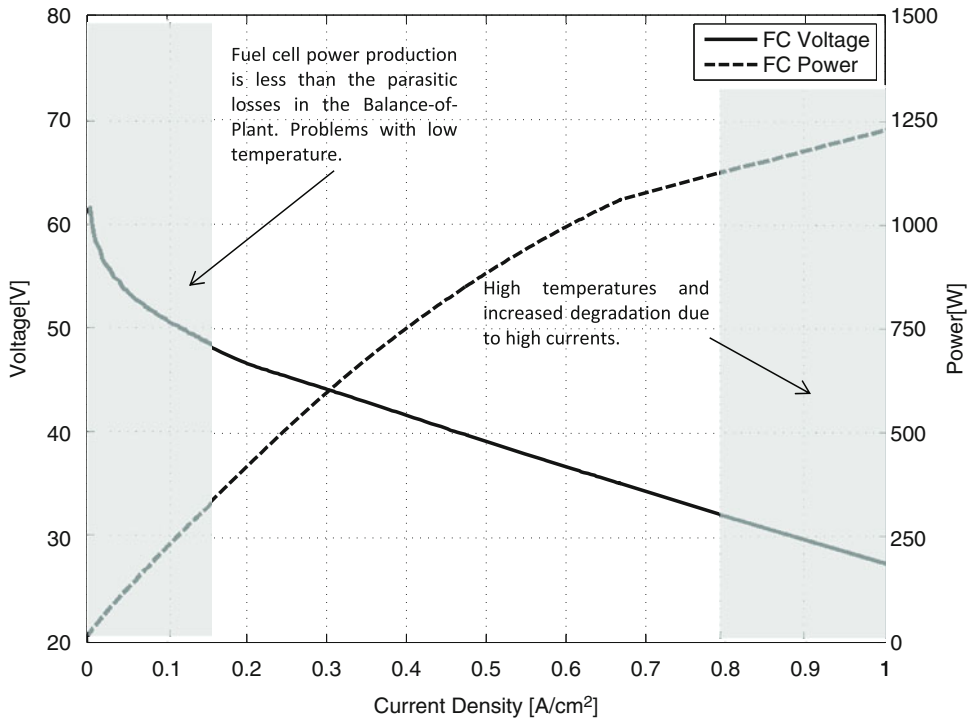


Fig. 21.13 Illustration on polarization and power curve of the problematic regions of operation from a system point of view

for a situation to enable it where more power is needed. Alternatively, and depending on the application the system could be put into a standby mode ensuring that it is always ready to deliver power when needed. In the other extreme, there is a certain limit as to how high currents are advisable to draw from the system. The subsystem cooling the fuel cell stack needs to be able to handle the high losses at these operating points, and in a similar way, for reformer systems, the required heat needs to be added to the reforming reaction in order to keep the correct reformer temperature. The fuel evaporator could also lose some of its heating abilities at very high flow, moving some of the superheating of the evaporated fuel into the reformer, requiring even more heat. The reformer catalyst volume will also at particularly high loads have problems converting the fuel, and the amount of unconverted fuel in the anode inlet of the stack.

21.6.2.1 Output Power Control

Proper control of the output current and power of the systems are one of the key areas in ensuring long and reliable lifetime. A DC/DC converter on the fuel cell output is a critical component when it comes to limiting the output current of the fuel cell stack, hereby protecting it from some of the mentioned undesired operating conditions. Figure 21.14 shows a typical configuration of a hybrid electrical system, where the fuel cell is charging the battery pack on-the-fly. As long as the available fuel cell power covers more than the average power consumption drawn from the battery pack, the system will see significant increase in run-time at a fairly low cost per kWh because of the low investment cost in additional fuel tank versus adding more batteries.

Using the fuel cell DC/DC converter it is possible to introduce current limits avoiding too low or too high currents, but more importantly, when working with reformer systems, limits to

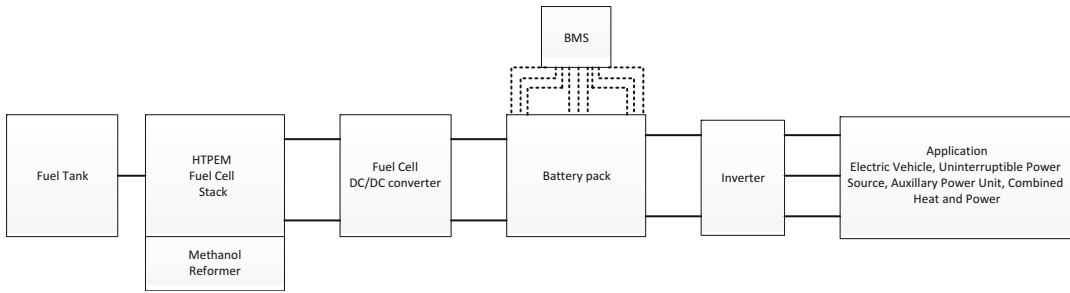


Fig. 21.14 Example of fuel cell reformer system hybrid electric power system

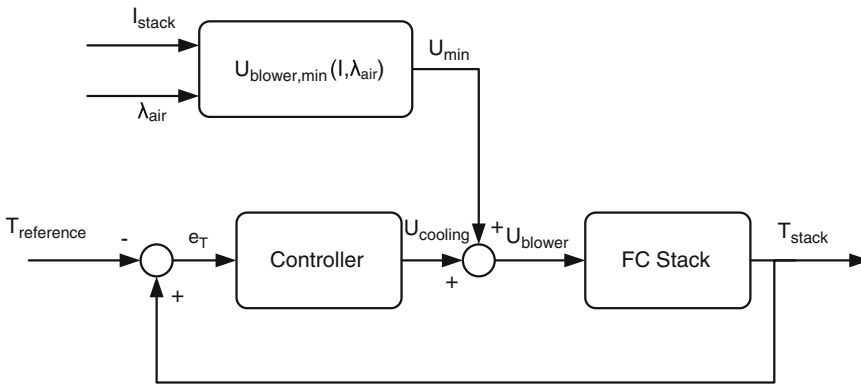


Fig. 21.15 Control structure for control of cathode air cooled HTPEM fuel cell stack. Reproduced from [57] with permission of Elsevier

how fast load transitions can be made, i.e., current ramp limitations. Hard restrictions on the current through the DC/DC converter will diminish the load following capabilities of the fuel cell system, but on the other hand, this can in turn lead to more stable system operation, ensuring that the system receives the right amount of fuel, avoiding critical starvation and high burner temperatures. In the case of the fuel cell system acting as a battery charger, the DC/DC converter simply has a preprogrammed charging curve, depending on the particular type of battery, and chemistry. This ensures safe operation by starting the charging at, for example, a certain threshold voltage or state-of-charge, and stopping the system again upon going through a full charge cycle.

21.6.2.2 System Temperature Control

The type of temperature control used in a fuel cell system depends on the type of fuel cell in the system. If the fuel cell is cathode air cooled, the blower which also supplies the cathode process air flow is used to cool the fuel cell stack. In such a control structure, it is important to include a blower model which can predict a minimum blower set point to ensure that a certain minimum stoichiometry is respected at all times. Figure 21.15 shows a diagram of such a control system.

The controller in such a system can be any kind of controller, e.g., a PI, PID, PID with a feed forward term, or any advanced control structure.

When performing temperature control it is important to have good and reliable temperature measurements. It is also important to be aware that temperature gradients might exist in the fuel cell, meaning that the temperature locally might

be higher or lower than the measured temperature, which could damage the fuel cell. This problem can be solved by using a temperature set point, which has a certain safety margin to critically high or low values. An alternative is to implement a thermal model of the fuel cell in the controller, in order to choose an appropriate temperature set point, for a given set of operating conditions. If several temperature measurements exists, the control variable for the controller can be chosen to be either an average of these, the highest or the most representative.

21.6.2.3 Control of Methanol Reformer Temperature

In a highly integrated system like the one in Fig. 21.5 it is important to have a stable and efficient temperature control, both in stationary and dynamic operation. The most difficult temperature to control is that of the reformer. This is because the heating power for the reformer is not

supplied directly, but through the burner, which is supplied with varying amounts of exhaust gas from the fuel cell anode.

One way of remedying this issue is to exploit the fact that thermal mass of the burner is much smaller than that of the reformer and use a cascade control structure. Figure 21.16 shows a diagram of such a control structure from [58]. Here the inner, faster, control loop controls the burner temperature by varying the air supply to the burner. The outer, slower, control loop controls the reformer temperature by changing the set point for the burner temperature.

The structure used for the two controllers can be any of those available in literature, such as PI, PID, PID with a feed forward term, or any advanced control structure. Another, simpler, control structure is to omit the inner burner temperature controller and use the outer controller to control the reformer temperature by varying the burner air supply.

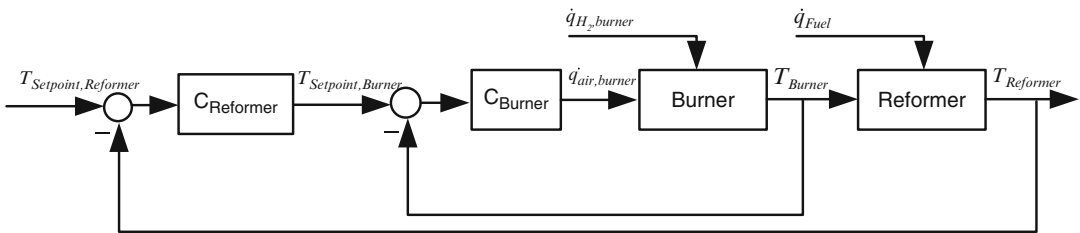


Fig. 21.16 Cascade control structure of reformer temperature. Reproduced from [58] with permission of Elsevier

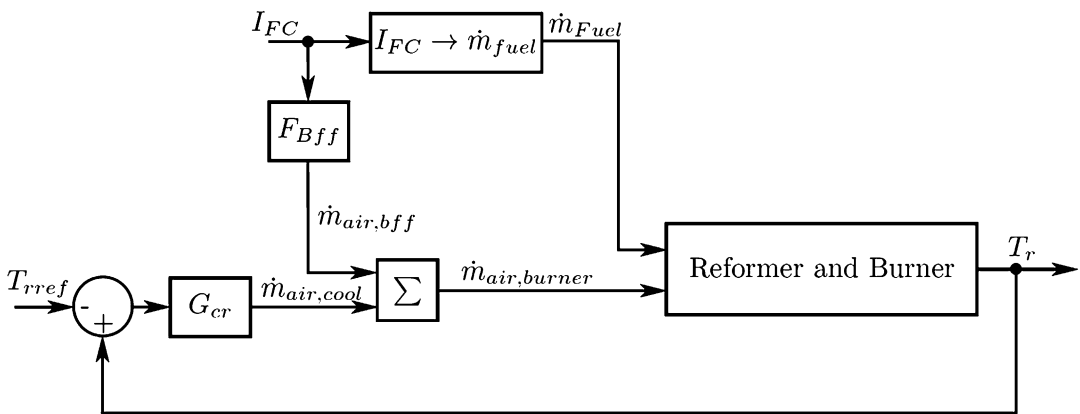


Fig. 21.17 Feed forward structure for a reformer temperature controller

As with the fuel cell temperature, the controller output which is necessary at a high output power is very different than that which is necessary at a low output power. It therefore makes sense to use a feed forward model necessary controller output in the controller for the reformer temperature. As the amount of fuel coming into the reformer and the burner relates to the current of the fuel cell, it makes sense to use the fuel cell current as the input to the feed forward model. Figure 21.17 shows a block diagram of a feed forward control structure, where the fuel cell current is passed into a feed forward model, F_{Dff} , which calculates an estimated necessary cooling mass flow. This mass flow is then summed with a correction from a controller to give the burner air mass flow.

The feed forward model can be made more advanced by adding other measurable inputs, such as the ambient air temperature and humidity, which affects the cooling power of the supplied air.

21.6.3 System Shutdown

As mentioned earlier in this chapter, HTPEM fuel cells are subject to severe carbon corrosion during open circuit operation. Therefore a shutdown strategy is necessary to avoid this during system shutdown.

One such strategy, which is used often, is to shut off the fuel supply for the fuel cell and draw a current from the cell until all the residual fuel in the cell is used. The current is typically drawn by a bleeder resistor, which can be connected to the terminals of the fuel cell stack. The fuel cell can then be cooled down to a temperature where carbon corrosion is not an issue.

When integrating a HTPEM fuel cell into a complex system, like a methanol reformer it can be advantageous or even necessary to implement more advanced control algorithms or models in the control systems. The next chapter describes some of the possible issues and a possible solution to them.

21.7 Advanced Control Strategies Using ANFIS Modelling

Control of different system states is manageable to a certain extent, as long as sensors can be placed to monitor the states in question, such as pressure, temperature, and humidity. Many internal states in fuel cell systems are, however, often not measured due to the available sensors being impractical either due to very high costs, or volumetric, weight or data acquisition constraints. If monitoring or measurements of such non-accessible states are required, either a modelling-based approach or an ex situ experimental characterization is the only possibility of predicting these states, and in turn controlling them. In high temperature PEM fuel cell systems using a reformer, some of the critical system states are CO concentration of the anode gas and the hydrogen mass flow into the fuel cell stack anode. The reason for calling them critical is that they both have a direct impact on stack lifetime and performance. Due to the complex dynamics of the fuel delivery system of a methanol reformer system, such as the ones shown in Figs. 21.1, 21.4, and 21.5, it is not trivial knowing how fast load changes can be allowed. The challenge is threefold; firstly, it is important to know exactly how long time passes before fuel is available in the anode when the fuel pump flow is increased. If the load on the fuel cell stack is changed too quickly, the fuel cell stack will experience anode starvation and the accelerated degradation related to this. Secondly, if the load is decreased too quickly, high amounts of hydrogen will be entering the fuel burner, which could lead to extreme temperatures and possible burner meltdown. Lastly, the varying reformer output composition, which is a function of space velocity, temperature, and fuel concentration, also makes the exact prediction of hydrogen content, and therefore anode stoichiometry, complex and this has a direct influence on the system efficiency, because excess fuel simply will be combusted in the burner. One approach to address these challenges is using Adaptive

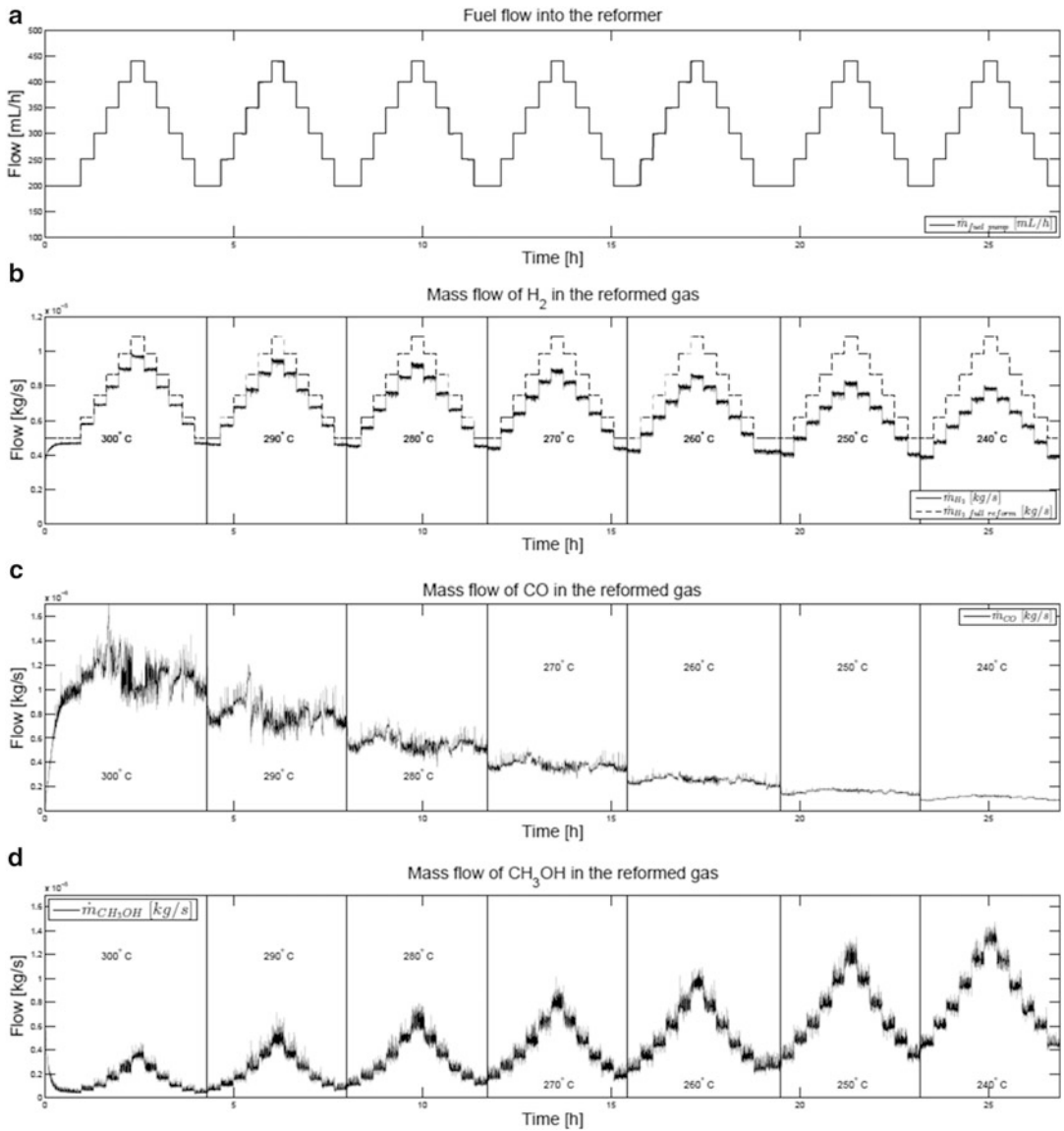


Fig. 21.18 Output reformer mass flows, fuel flow and reformer temperature from ex situ characterization tests on methanol reformer. Reproduced from [60] with permission of Elsevier

Neuro-Fuzzy Inference System models first described in [59] and used in [60, 61]. This approach has proven to be a powerful means of using detailed experimental characterization knowledge online for system control. The methodology has been tested on a Serenergy H3-350 methanol reformer HTPEM fuel cell system, and includes characterizing the steam reformer ex

situ in a dedicated setup [60], yielding a full performance map testing it in all relevant operating points. An example is shown in Fig. 21.18, where changes in concentrations are seen while going through different steps in pump flow and reformer temperature.

The shown measurement indicated the CO concentration increasing with increasing

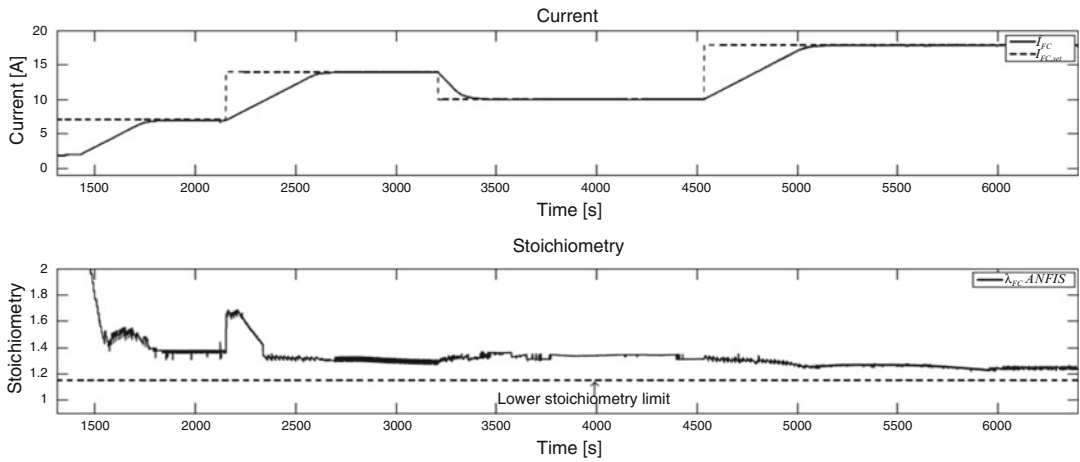


Fig. 21.19 Figure shows the predicted stoichiometry of implemented ANFIS model during load variations. Reproduced from [60] with permission of Elsevier

temperature, and the opposite occurring for residual methanol concentration. Based on such experimental data, an ANFIS model can be trained to behave as the experimental data. The model combines fuzzy logic with neural network theory to create a series of mathematical equations to predict the steady-state behavior of the reformer output composition depending on temperature and fuel flow [60].

The implementation of the model yields a possibility of monitoring the stoichiometry of the anode, as shown in Fig. 21.19 where the stoichiometry during a series of changes in fuel cell current is seen.

In the shown figure, it is clear that the stoichiometry is changing during the different operating points: This happens because the fuel flow is calculated based on the desired fuel cell current using a linear relation and assuming a full reforming of the fuel. This calculation is usually done by calculating the necessary hydrogen production according to (21.5), where $\dot{m}_{H_2,FC}$ is the needed hydrogen flow, λ is the wanted stoichiometry, N_{cell} is the number of cells in the fuel cell, and F is Faradays constant.

$$\dot{n}_{H_2} \left[\frac{\text{mol}}{\text{s}} \right] = \frac{\lambda \cdot N_{cell}}{2 \cdot F \left[\frac{\text{C}}{\text{mol}} \right]} \cdot i_{FC} \left[\frac{\text{C}}{\text{s}} \right] \quad (21.5)$$

From the steam reforming reaction it is known

that 1 mol of methanol yields 3 mol of hydrogen. The necessary methanol flow into the module then calculated according to (21.6).

$$\dot{n}_{CH_3OH} \left[\frac{\text{mol}}{\text{s}} \right] = \frac{\lambda \cdot N_{cell}}{6 \cdot F \left[\frac{\text{C}}{\text{mol}} \right]} \cdot i_{FC} \left[\frac{\text{C}}{\text{s}} \right] \quad (21.6)$$

Using a model-based approach with, for example, an ANFIS model that predicts the hydrogen production under a given set of conditions and the stoichiometry can then be controlled more precisely.

Another way of using such advanced models is to examine the dynamics of the system and including it in the control structure. Often reformer systems, and fuel cell systems in general, are used in hybrid electric systems, because they are good candidates as range extenders, providing cheap energy compared to expanding battery capacity, because increasing tank size on a reformer system is much more cost effective compared to adding additional batteries. By detailed analysis of optimizing the balance between battery and fuel cell power it is possible to find optimized solutions, to specific applications. One of the disadvantages of increasing system complexity by adding reformers is the added thermal dynamics of increased masses, pipe volumes, etc. adding to the dynamic behavior of the system, thus

affecting the fuel cells load following capabilities. One typical method for handling such delays, and ensuring safe system operation, is to put a rate limiter on the current set point for the fuel cell stack. This requires a DC/DC converter able to control the output power from the fuel cell stack, which in many cases is available. A current ramp limitation would typically allow the stack to change load point in a matter of, for example, 30 s instead of instantaneously, but in order to reintroduce load following capabilities detailed knowledge is needed on the dynamics of the system.

21.8 HTPEM Fuel Cell System Diagnostics

The commercial success of not only HTPEM fuel cells, but fuel cell systems in general depends on their performance, reliability, durability, and competitiveness compared to other power generation devices. A large part of this can be improved by advanced state-of-health monitoring and the ability of diagnosing problems before they occur. With the implementation of such features, the systems can be protected from additional destructive operation due to failures in, for example, the fuel cell stack, in system components and in sensors. If a failing fuel cell stack or other system components can be replaced during already planned maintenance

visits, operating costs could be reduced and system on-time increased by avoiding system breakdown, damage of other system components and un-planned service visits. Figure 21.20 shows some of the primary components of a HTPEM fuel cell system, and the usual monitored states. Of the many methods existing, a lot of focus has been on diagnostic issues and state-of-health of the fuel cell stack as one of the more critical components of the system.

Several diagnostic methods exist that are able to monitor the performance of, for example, the fuel cell stack, and possibly conduct an in situ diagnostic method able to characterize and isolate the particular error, and implement a proper mitigation strategy for compensating for the problem, or safely shut down the system. Some of the more common practice diagnostic methods for analyzing stack behavior are

- U, I characterization, open circuit voltage, polarization curves
- Performance degradation over time
- Electrochemical Impedance Spectroscopy (EIS)
- Chronoamperometry, current interruption (CI)
- Total harmonic distortion analysis (THDA)

Measuring the voltage and current of a fuel cell is one of the most used characterization tools for benchmarking the performance of a fuel cell.

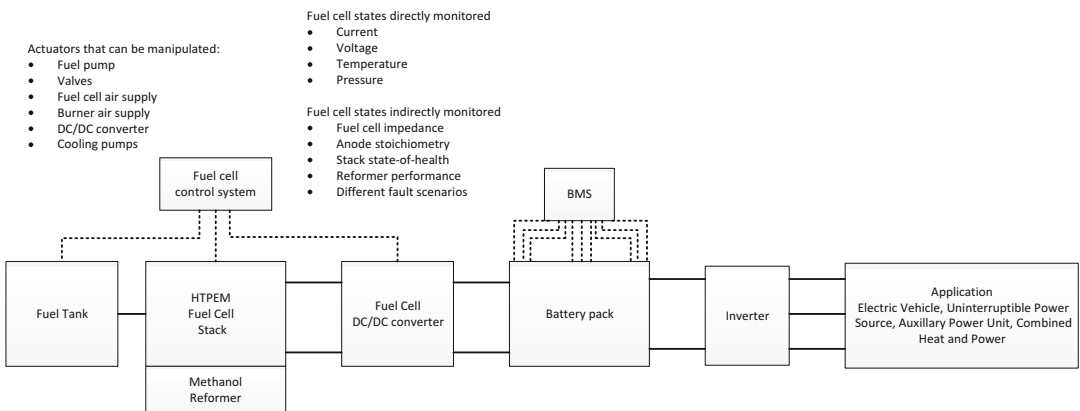


Fig. 21.20 Typical configuration of an electric hybrid system using a HTPEM fuel cell

Polarization curves further detail such measurements by including the current dependence on the voltage performance of the fuel cell by examining the voltage at different steady-state currents, different temperatures, etc. Figure 21.10 shows a set of polarization curves made on a 45 cm² BASF MEA. The fuel cell dependence on temperature is visible, showing increasing performance with increasing temperatures.

On running systems, polarization curves can be constructed by making a controlled slowly ramped current ensuring the system is in a pseudo-steady state. This is only possible in systems where fuel cell stacks output power is conditioned using a DC/DC converter or other power electronic component, and where the system shortly is allowed to conduct such a diagnostic routine. In hybrid electric system this is often easy because the fuel cell power is used to charge a battery pack and the output power can briefly be manipulated. In applications where the fuel cell power is dominating and the power directly needed a better approach is to look at the voltage

as a function of current for a short amount of time where a partial polarization curve often can be evaluated.

In order to capture the dynamic nature, and electrical characteristics of a fuel cell, methods like chronoamperometry or current interruption techniques are an option. The method is able to separate the contributions of ohmic and non-ohmic processes and capture the dynamic voltage response during a few steps in the current. A generic plot of the expected voltage and corresponding current step signal is shown in Fig. 21.21.

The dynamic electrical response of the fuel cell could include information on temperature, gas quality, degradation state, etc. and the method can be implemented using simple resistors and switches. Using steps to characterize and diagnose certain anomalous behavior is a common system identification tool and can also be applied to other aspects of examining HTPEM fuel cell system behavior. Figure 21.22 shows an example in a HTPEM fuel cell system, measuring on a HTPEM short stack, where a step is induced in the anode fuel stoichiometry, the response on the fuel cell voltage can be registered and depending on the stack state-of-health or the status and quality of the anode fuel supply system, it could be possible to determine certain errors in a system or adjust various system parameters to mitigate the potential problems. In a similar way many other fuel cell system components can also be manipulated and be part of a larger system diagnostic procedure in order to identify or isolate certain system faults.

Electrochemical impedance spectroscopy (EIS) has been used extensively to characterize HTPEM fuel cells [13], and also stacks [62, 63], in order to increase the understanding of the different mechanisms occurring within the fuel cell and have a means for quantifying the changes occurring. Often the results of EIS are evaluated in the frequency domain, analyzing Nyquist plots and bode diagrams, looking at the changes occurring over the entire range of frequencies. Equivalent electrical circuits are often used to fit models representing the electrical behavior of the fuel cell using different

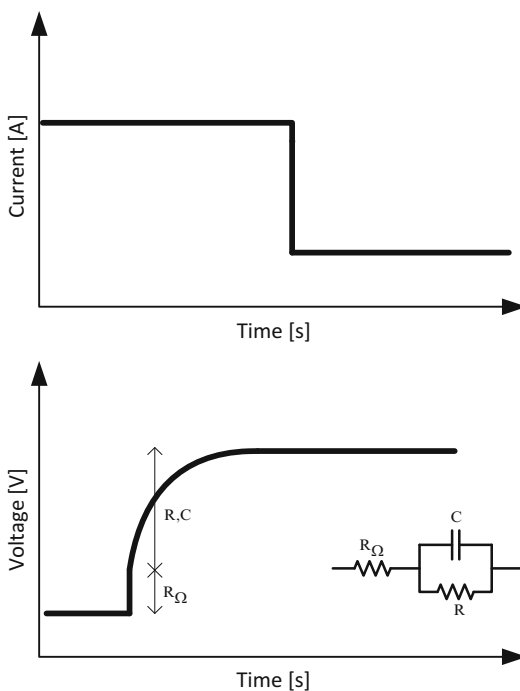


Fig. 21.21 Fuel cell voltage response during current step

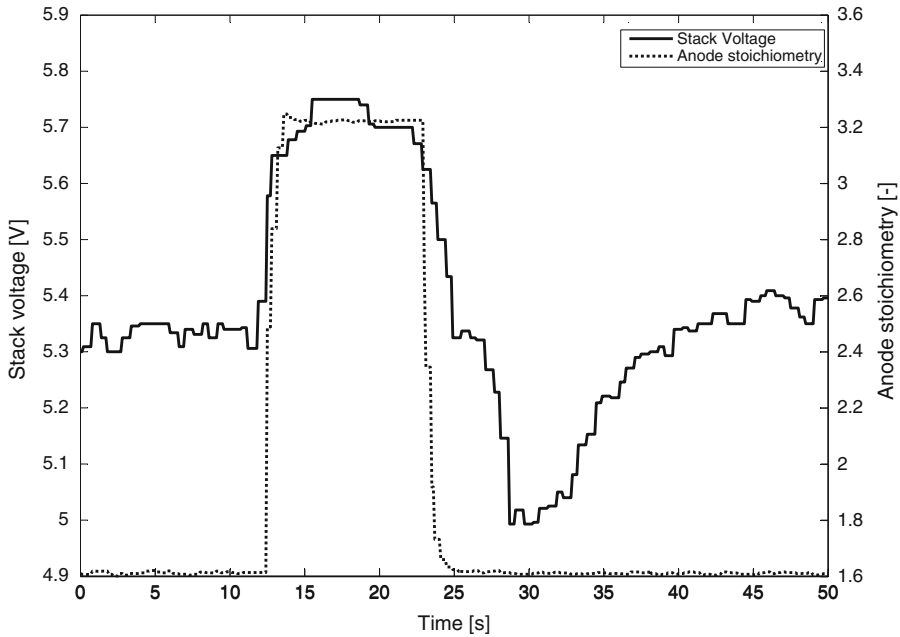
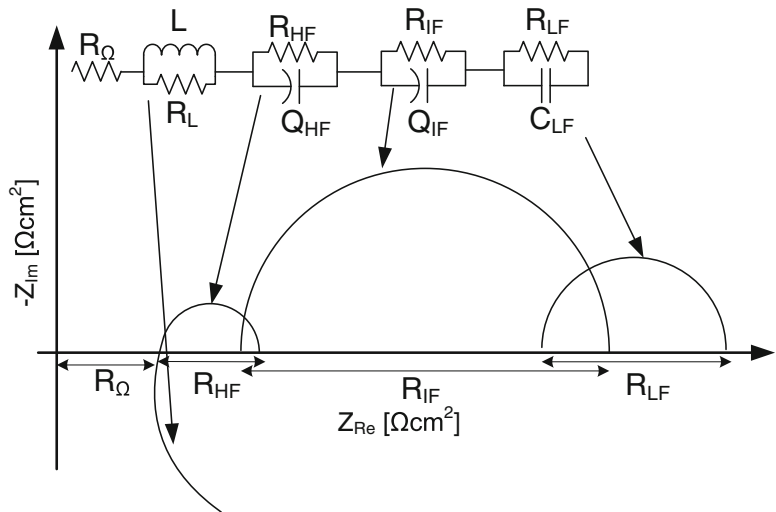


Fig. 21.22 HTPEM short stack voltage response to a step in the anode stoichiometry

Fig. 21.23 Example of impedance spectrum for the shown equivalent electrical circuit. Reproduced from [13] with permission of Elsevier



networks of resistors, capacitors, inductors, and more exotic elements such as constant phase, Warburg elements and similar (An example can be found in Fig. 21.23).

Examples exist of, for example, using EIS as a monitoring tool for the activation of HTPEM fuel cells [64–66]. Using a single frequency also

provides a good tool for quantify stability and the difference between the use of, for example, different types of bipolar plate material. In this case, two phenolic resins, a surface treated graphite material and a gold plated stainless steel plate. In this case only the 1 kHz frequency was monitored and proved as a good tool for

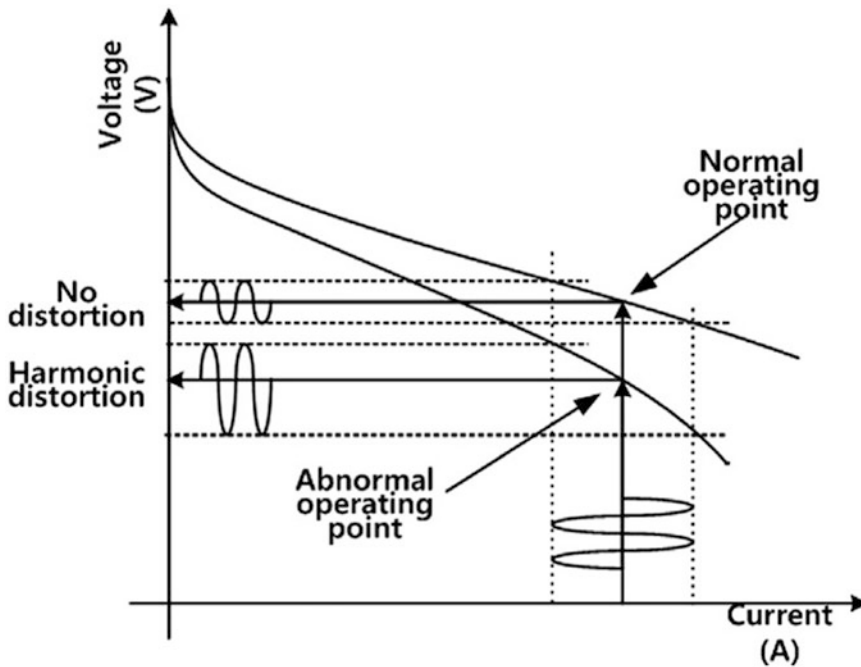


Fig. 21.24 Example of current and voltage behavior on polarization curve in different situations. Reproduced from [67] with permission of Elsevier

characterizing the differences in the performance of the plate material. Although EIS is a somewhat more complicated measurement technique, the use of it online in systems could be an interesting tool that in some cases possibly could quantify the propagation of certain fault scenarios or be part of isolating a particular error occurring.

Total harmonic distortion is another diagnostic tool usable in situ, the general method includes superimposing a load current with a harmonic content and afterwards analyzing the total harmonic distortion of the fuel cell voltage. Used in HTPEM fuel cell diagnostics, it is possible to, for example, identify anode and cathode starvation that is distinguishable using total harmonic distortion analysis (THDA) (Example of method is visualized in Fig. 21.24) [67].

Fuel starvation in HTPEM fuel cells is a critical stressor which should be avoided at any cost due to the increased carbon corrosion of the cells under such conditions.

21.9 Applying Diagnostic Procedures

Many diagnostic methods exist, involving either manipulating the current or voltage delivered from the stack, introducing specialized power electronics circuits, either added to the system or preferably as an added feature to the already existing DC/DC converter, conditioning the power delivered by the fuel cell stack [68]. From a cost point of view, adding features to existing components is a more viable method than introducing new and expensive components.

Usually the different diagnostic tools such as current interruption, total harmonic distortion, and impedance spectroscopy or other tools requiring signal analysis can require high speed sampling that is often not available in the cost optimized types of electronics that are used on commercial system for controlling and monitoring the fuel cell systems. A good understanding of the failure patterns of the critical components and their causality is needed in order to

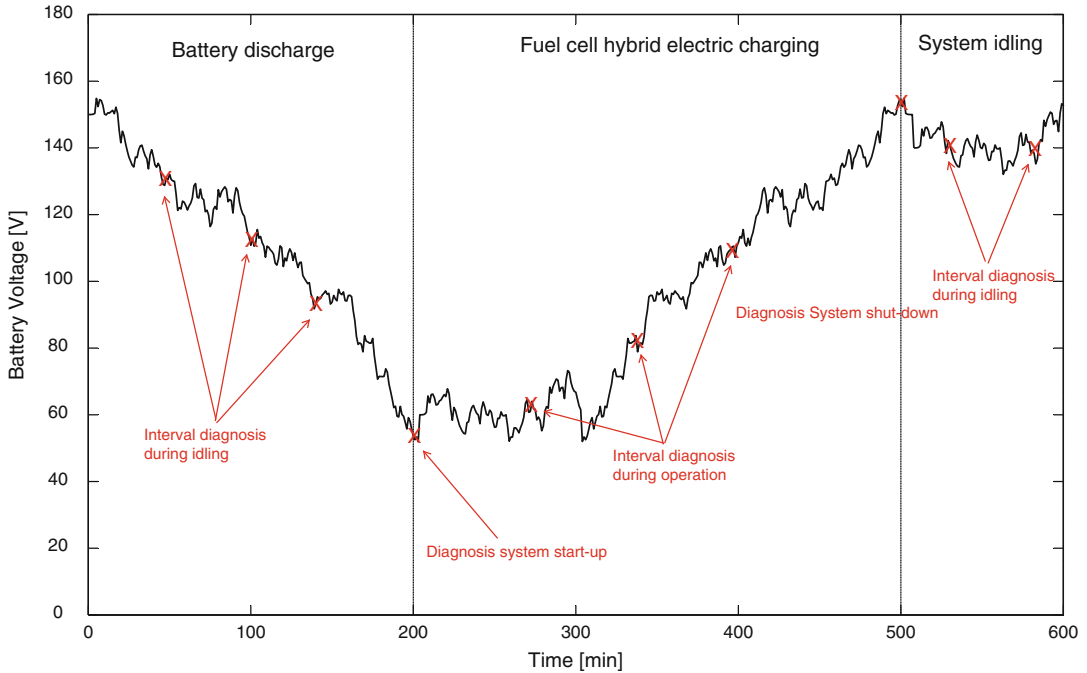


Fig. 21.25 Examples of planned and continuous activation of diagnostic strategies during various fuel cell states

implement tools able to monitor various fault, states-of-health and remaining useful lifetime of the system. In the more developed Nafion-based systems, examples exist of promising diagnostic methods that are able to predict possible problems related to flooding or drying of a stack. Impedance spectroscopy can be used to analyze the hydration status of idling fuel cell stacks in order to predict whether or not re-humidification is needed before start-up [69]. Similar techniques could possibly be used in HTPEM fuel cell system to analyze phosphoric acid quality, membrane conductivity, to update state-of-health and lifetime algorithms.

Several diagnostic methods exist, their relevance often depends on the particular diagnostic results that are desired, and this in turn depends on the specific application. Mainly *in situ* or *in operando* methodologies, such as CI, THDA, and EIS, are relevant for systems that are operating, and besides fault detection, state-of-health monitoring it is desired to also possibly use these techniques to continuously update parameter-based models used for predicting various internal states and updating controller parameters,

everything being executed while system is running. Offline, *ex situ* techniques can give valuable information about the operation history of a fuel cell but are usually more suited for characterizing, performance characterization, different physical quantities, and mechanisms or for quality assessment and lifetime analysis.

The particular timing of when a certain diagnosis in a fuel cell system is conducted can vary from system to system, some techniques require steady-state operation, and others can operate on being fed with historical data of the system performance. Looking at HTPEM fuel cell systems with fuel reformers, they have some interesting possibilities, as mentioned before, when working in electric hybrid systems where a battery pack is being charged by the fuel cell system. In such cases it is possible to implement several different diagnostic strategies because it is often possible to separate the fuel cell power delivery from the hybrid electric system power delivery. An example is shown in Fig. 21.25 of some of the different strategies and situations where a diagnostic procedure could be executed.

The figure shows the battery voltage in a hybrid electric fuel cell system, where, for example, a fuel cell acts as a run-time extender, and providing energy from a given fuel. In the case, three different operating modes are visualized.

- *Battery discharge mode:* The battery is running in discharge mode with the fuel cell system either off or idling. In such cases a fuel cell diagnostic system could perform various performance tests or failure diagnostics, the advantage being that the fuel cell stack, and components are available for manipulation and not necessarily required to support energy production in the system. Performance tests of blowers, valves, and pumps could be performed depending on which sensors are present. The reaction of various levels, flows, pressures, concentrations, temperatures, etc. on given cycling procedures of these actuators. A reference set of normal response of the different sensors can usually be identified, and in case of differences to these reference responses, either system errors can be activated rendering the system unusable until service has been performed or the various control parameters, set points, and state-of-health algorithms can be adjusted to ensure optimum system performance. Usually the fuel cell stack will not be able to deliver power because of the absence of fuel, but small diagnostic circuits could still analyze the conditions of the fuel cell stack as mentioned before.
- *Fuel cell start-up:* Just before, during, or after fuel cell start-up a diagnostic routine could be initiated to update control parameters, system monitoring models, lifetime algorithms or simply compare system behavior to a reference case of the expected normal behavior or the response from a recent start-up. This could be done using electric stimulation of the fuel cell stack in some of the earlier mentioned methods, or by analyzing heating behavior of the system start-up response.
- *Fuel cell charging:* In fuel cell charging mode the fuel cell is actively providing power, either at a fixed operating current, voltage or power or using a load following algorithm adapting to user interaction with the application in question or the power drawn from the battery pack. In the different situations various diagnostic approaches are possible. In the case where, for example, the current is constant, both EIS and current step procedures could be used that could provide information on cell performance, degradation as described above. Diagnostics can be more challenging when the power is changing dynamically, EIS is difficult to apply in such cases because the DC component of the voltage and current is dynamically changing and could move into highly nonlinear operating areas of the polarization curve. Furthermore with changing current and voltage, temperatures also change proving it difficult to get proper steady-state measurements. Diagnostics during such operating mode need special considerations and careful signal analysis due to complex nonlinear behavior.
- *Fuel cell system shutdown:* Before shutting the system down, diagnostic tools could be used to extract information of the performance of the fuel cell system at the moment of shutdown, later comparison of that performance could yield important information regarding the state of the system prior to or after start-up.
- *Fuel cell system idling:* After system shutdown a period of idling or complete power down can be experienced. Depending on the application in question different approaches are relevant. In systems that undergo long periods before start-up is required, and where, for example, “critical power” is delivered, it becomes relevant to periodically check the responsiveness of the system either by planned start-ups or by using a diagnostic approach able to check the state-of-health of the system and possibly detect potential malfunctions or possible service requirements.

Diagnostic tools become more and more relevant as HTPEM fuel cell systems are

commercialized. They can be usable in fault detection, optimization of system operation, efficiency, and reliability. Different regimes of fuel cell system diagnosis exist, some are related to short term time constant and need to be able to identify and isolate issues within seconds, others use minutes and hours of performance data to predict possible problematic behavior in the long term. Mitigation strategies can also have impact on different times scales, some problems require immediate action and failure handling, other perhaps initiate follow up procedures during next maintenance check others adapt the system controls to the changing behavior over time, to ensure robust behavior over the entire lifetime of the systems.

HTPEM fuel cells are still at an early stage when it comes to the development and implementation of diagnostic methods for monitoring the fuel cell system state-of-health, the identification of potential faults leading to failure or diminished lifetime, and the mitigation of different strategies to avoid severe problems, adapt system control to changing performance, or simply acknowledge the need for maintenance.

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