

Symmetric Stack Model of a Molten Carbonate Fuel Cell (MCFC) with Indirect Reforming

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Abstract: A model of a Molten Carbonate Fuel Cell (MCFC) stack with internal reforming is presented. It describes the concentrations in the gas phase, the temperatures and the current densities in this highly integrated system. The differential equations, the boundary conditions as well as the coupling equations used in the model are presented. A strategy to solve the system of partial differential equations is outlined and the simulation results are discussed.

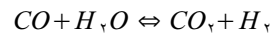
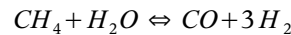
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1. Introduction

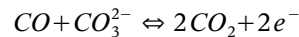
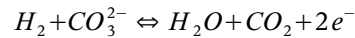
Fuel cells are an efficient technology for the efficient generation of electrical power. The Molten Carbonate Fuel Cell (MCFC) – a high temperature fuel cell – is suitable for the co-production of electricity and high-graded heat in stationary fuel cell power plants.

The working principle of this fuel cell type is shown in Fig. 1. A variety of fuel gases can be used: natural gas, gas from bio mass fermentation, gasified coal or waste gas. The fuel

gas has to be reformed before it can be used for electrochemical conversion. The reforming can be done either in an external reformer (ER), in a special reforming unit attached to the fuel cells in the stack called the Indirect Internal Reformer (IIR), or in direct neighborhood to the anode of the fuel cell (Direct Internal Reforming, DIR). The methane reforming reaction and the water gas shift reaction are considered:



The primary fuel cell consists of the anode, the molten carbonate electrolyte and the cathode. At the anode electrode, the electrochemical oxidation of hydrogen and carbon monoxide takes place:



The exhaust gas of the anode is completely burned with air in a catalytic combustion chamber. After that, the gas is redirected into the cathode gas compartment. Here, the carbonate ions needed for these reactions are produced by

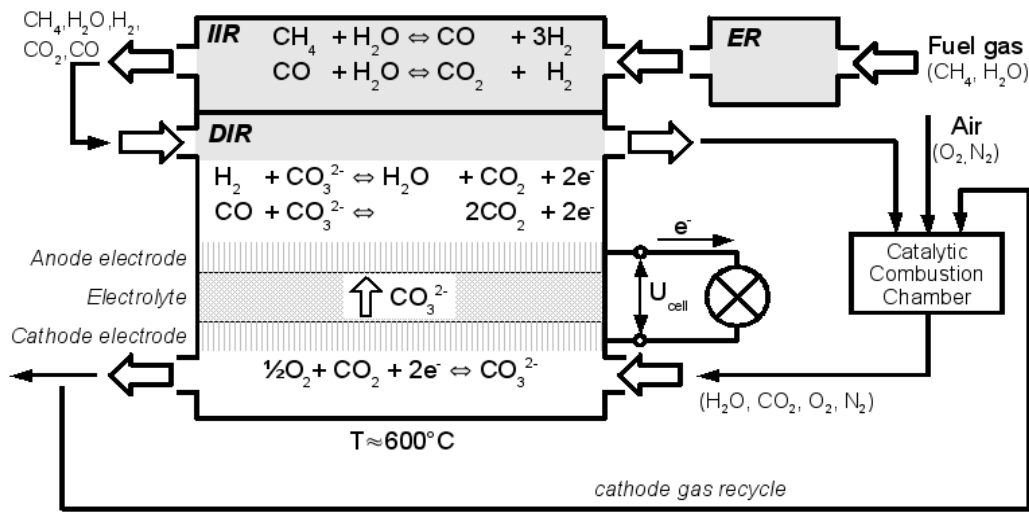
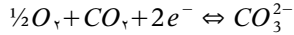


Figure 1: Working principle of a Molten Carbonate Fuel Cell.

the electrochemical reduction of carbon dioxide at the cathode electrode:



The reaction system is closed by the electrons, which move from the anode to the cathode in an external circuit.

Within the MCFC system, all components strongly interact with each other. On the one all gas compartments are connected by the mass flow. On the other hand the thermal interaction between the heat sources, especially the electrochemical reactions, and heat sinks – the reforming reactions – has to be taken into account. Furthermore the charge balance couples the electrochemical reactions at the anode and cathode electrodes.

The temperature is a key variable to describe the state of the fuel cell system. But a measurement of the temperature is often not possible. Wherefore numerical simulations are needed.

2. The Stack Model

Within the MCFC power plant, 342 fuel cells are arranged in a fuel cell stack. After each 8th

fuel cells one reforming unit is inserted into the stack. A numerical simulation of the entire MCFC stack would require a huge numerical effort. Therefore the stack is divided into smaller parts taking into account the symmetry in stack direction. Such a symmetric part consists of ½ reforming unit and four fuel cells. The structure is shown in Fig. 2.

The reforming unit is attached to the first fuel cell. It is arranged in a counter flow configuration with the anode gas compartment of this cell. Between the anode and cathode gas compartments of each cell, a cross flow configuration is used.

In addition to the above mentioned components, the model further includes a heat exchanger, the catalytic combustion chamber and a reversal chamber.

2.1 Assumptions

Besides the symmetric boundary conditions on the left and right hand side of the model, additional assumptions are used for the modeling of the symmetric MCFC stack:

- Ideal gases.
- Isobaric conditions.

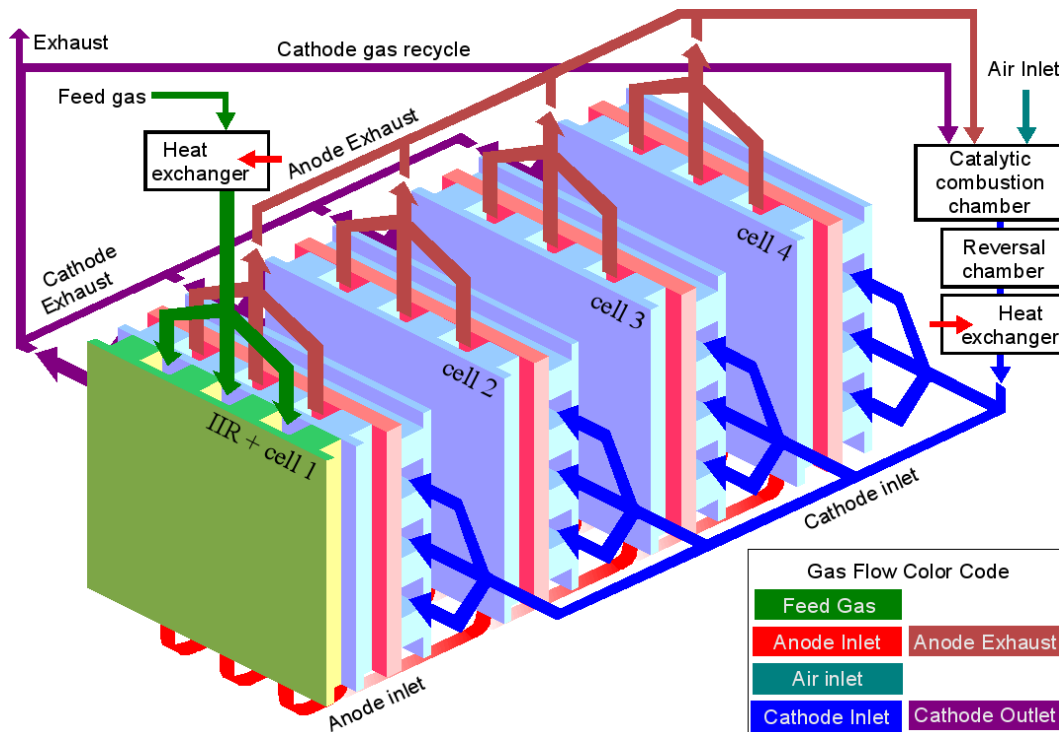


Figure 2: Structure of the symmetric MCFC stack model. It includes four fuel cells (blue and red) and an additional Indirect Internal Reforming unit (green), attached to the first cell. The gas flow within the stack is indicated by the arrows.

- All solid parts of a fuel cell are combined in the solid phase, which has an average heat conductivity.
- There are no concentration, temperature or velocity gradients perpendicular to the cell plane. This reduces the geometry of the different components to a 2D structure.
- For the reforming reactions, simple power law kinetics are used and the electrochemical reactions are described by Butler-Volmer kinetics.

2.2 Governing Equations

For the mathematical description of the symmetric MCFC stack, ordinary differential equations (ODE) and partial differential equations (PDE) are used. In the following, the basic structure of the model is discussed. A detailed derivation of the equations can be found in the literature [1,2,3].

The model is formulated in terms of dimensionless parameters. Therefore the model geometry represents a square with the dimensions 1x1. Within this 2D geometry, the equations for the reforming unit (14 PDEs) and the fuel cells - the anodes (12 PDEs each), the solid phase with the equations for the electrical potential (3 PDE and 1 ODE each) and the cathodes (10 PDEs each) – are defined. Additional ODEs are needed for the heat exchangers and the reversal chambers which are considered as spatially lumped reactors. The heat exchange in stack direction as well as the mass transport within each fuel cell are implemented using source terms in the corresponding equations.

Eq. (1) describes the convective mass transport in terms of the molar fraction X_i and Eq. (2) the convective energy transport within the gas compartments using the dimensionless temperature ϑ . The term on the left hand side of both equations accounts for the accumulation of mass or energy, respectively. The first term on the right hand side represents the convective mass or energy transport while the second term describes the mass or energy sources due to the (electro-)chemical reactions. For the energy balance the heat exchange with the neighboring components is also included.

$$\frac{\partial X_i}{\partial \tau} = -\omega \nabla X_i + \sigma_{X_i}(X, \vartheta, \dots) \quad (1)$$

$$\frac{\partial \vartheta}{\partial \tau} = -\omega \nabla \vartheta + \sigma_{\vartheta}(X, \vartheta, \dots) \quad (2)$$

The profile of the dimensionless velocity ω within the gas compartments is calculated using Eq. (3). The velocity changes due to the volume increase by the reactions as well as the thermal expansion of the gas are taken into account.

$$0 = -\nabla \omega + \sigma_{\omega}(X, \vartheta, \dots) \quad (3)$$

Within the solid phases, the temperature is described by the heat conduction equation (Eq. (4)). Accumulation is taken into account by the term on the left hand side of the equation. On the right hand side the heat conduction and the heat sources – the electrochemical reaction at the electrodes and the ion conduction losses within the electrolyte – are considered.

$$\frac{\partial \vartheta_s}{\partial \tau} = \nabla (\nabla \vartheta_s) + \sigma_{\vartheta_s}(X, \vartheta_s, \varphi) \quad (4)$$

The definition of the charge balance is shown in Eqs. (5) and (6). The electrical potential depends on the concentrations within the anode and cathode as well as on the temperature of the solid phase. Additionally the integral of the cell current density has to be equal to the given cell current.

$$\frac{\partial \varphi}{\partial \tau} = i - i_a(X, \vartheta_s, \varphi) \quad (5)$$

$$I_{cell} = \int_{\zeta} i(\zeta) d\zeta \quad (6)$$

2.2 Boundary Conditions

The most important constraints within the model are the connections between the inlet and outlet of the different gas compartments along the gas flow path. Exemplary, the constraints for the reforming unit are shown below.

$$X_i = X_{i,in} \quad \text{on } d\Omega_{in} \quad (7)$$

$$\vartheta = \vartheta_{in} \quad \text{on } d\Omega_{in} \quad (8)$$

$$\omega = \omega_{in} \quad \text{on } d\Omega_{in} \quad (9)$$

At the inlet of the reforming unit, the composition of the gas, the temperature and the velocity is given (Eqs. (7) - (9)).

At the gas outlet, average values for the gas properties have to be calculated. Within these equations the dimensionless molar flow Γ and the dimensionless molar flow density $\gamma = \omega \vartheta$ is used instead of the gas velocity (Eqs. (10) - (12)).

$$\Gamma_{out} X_{i,out} = \int_0^1 [-\gamma X_i]_{\Omega_{out}} d\Omega_{out} \quad (10)$$

$$\Gamma_{out} c_{p,out} (\vartheta_{out} - \vartheta^r) = \int_0^1 [-\gamma c_p (\vartheta - \vartheta^r)]_{\Omega_{out}} d\Omega_{out} \quad (11)$$

$$\Gamma_{out} c_{p,out} (\vartheta_{out} - \vartheta^r) = \int_0^1 [-\gamma c_p (\vartheta - \vartheta^r)]_{\Omega_{out}} d\Omega_{out} \quad (12)$$

Within these equations, c_p is the heat capacity of the gas and ϑ^r the reference temperature.

For these constraints, the non-ideal boundary constraint mode is used to account for the flow direction of the gas, i.e. there is no dependency of the gas condition at the outlet on the gas flow in the following gas compartments.

Similar constraints are used for the inlets and outlets of the anode and cathode gas compartments.

3. Solving Strategy

Taking into account all differential equations, the model consists of 114 PDEs and 26 ODEs. These equations are highly coupled to each other due to the connection of the gas compartments via the gas flow, the thermal interactions between all parts of the model, especially in stack direction, and the corresponding electrochemical reaction at the anode and cathode of each fuel cell. Using a 7x7 mapped mesh and Lagrange-Quadratic elements, the model has 25.676 degrees of freedom.

Due to the complexity of the model, a direct solution of all equations is not possible. Therefore a 'start up strategy' for the numerical solution has been developed. The UMFPACK direct solver is used.

The model is solved in several steps, each step using the solution of the previous step as initial value. More equations are included in the solution process with each step. First, only the equations of the IIR are solved. In a second step the equations for the anodes of all four fuel cells are added. Following the gas flow direction, the cathode compartments are included in the next step. After that, only the temperature within the solid phase and the equations for the electric potential field are solved taking into account the gas properties calculated in the previous steps. In a final step, a solution of the entire model is calculated. To reduce the numerical effort, a coarser mesh is used for all calculations except for the last one.

The calculation time applying this solution algorithm is about one hour on a Dual Intel® Xeon CPU 3.20GHz. Up to 3.5 GB RAM are needed to solve the symmetric stack model.

4. Simulation Results

Fig. 3 shows the hydrogen molar fraction within the reforming unit (IIR) and the four fuel cells. Within the reforming unit, methane is converted to hydrogen by the methane reforming reaction. The hydrogen molar fraction increases from 0% to 20%. In the anode gas compartments, two processes occur. On the one hand hydrogen is produced by the reforming process, on the other hand hydrogen is consumed by the electrochemical reactions. Thus the hydrogen molar fraction within the anode slightly increases near the anode gas inlet and after that decreases towards the gas outlet.

For the operation of an MCFC, the maximum and minimum temperatures in the cells are highly relevant. These temperatures as well as the average cell temperatures are presented in Fig. 4. The simulation results show a temperature range between 635°C and 695°C in the solid phases of the symmetric stack model. Within one fuel cell, the difference between the highest and lowest temperature can vary between 20°C and 30°C. Taking into account the symmetry along the stack direction, the minimum and the average temperature clearly show a parabolic temperature profile between two reforming units. The maximum temperature of the third and fourth fuel cell differ from the expected parabolic profile. The reason can be

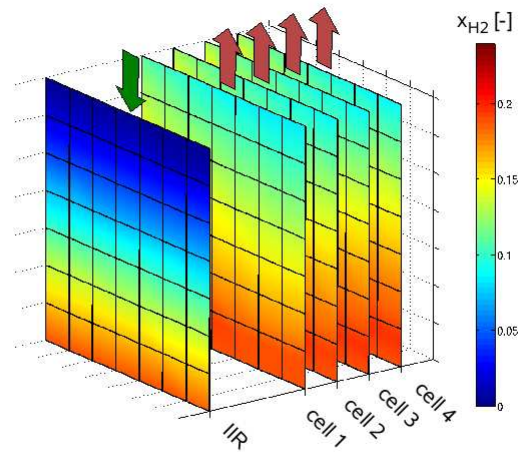


Figure 3: Hydrogen molar fraction within the reforming unit (IIR) and the anode compartments of the four fuel cells of the symmetric stack model. The arrows indicate the flow direction of the gas.

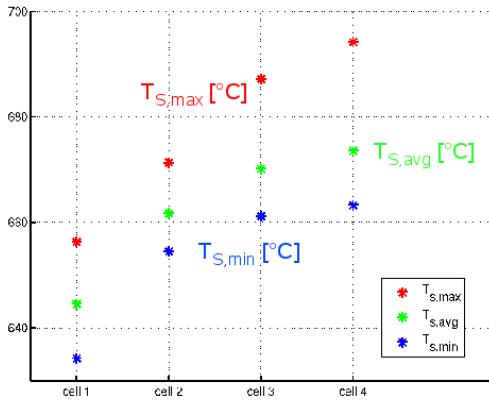


Figure 4: Minimum, average and maximum temperature within the solid phase of the four fuel cells.

found in the 2D temperature profiles of the solid phases of all four fuel cells (Fig. 5).

The highest temperature within the entire fuel cell stack can be found in the fourth cell at the top left corner – the outlet of the anode and

cathode gas compartments. This hot spot is the result of the convective energy transport within the gas compartments. The third fuel cell shows a similar temperature profile.

The cooling effect of the endothermic methane reforming reaction, taking place in the IIR, is visible in the temperature profiles of cell 1 and cell 2. The highest temperature within these fuel cells is located at the lower boundary. The high hydrogen concentration near the anode inlet leads to high electrochemical reaction rates, which release large amounts of heat resulting in a temperature maximum in that area.

For all four fuel cells, the lowest temperature can be found at the right hand side – the cathode inlet. The cathode gas is cold compared to the cell temperature due to the excess air added in the catalytic combustion chamber.

The temperature profiles show that the fuel cells within the stack are working at different operating conditions. On the one hand there are the fuel cells next to the IIR, which acts as a cooling device. These fuel cells have a nearly uniform temperature profile at temperatures of

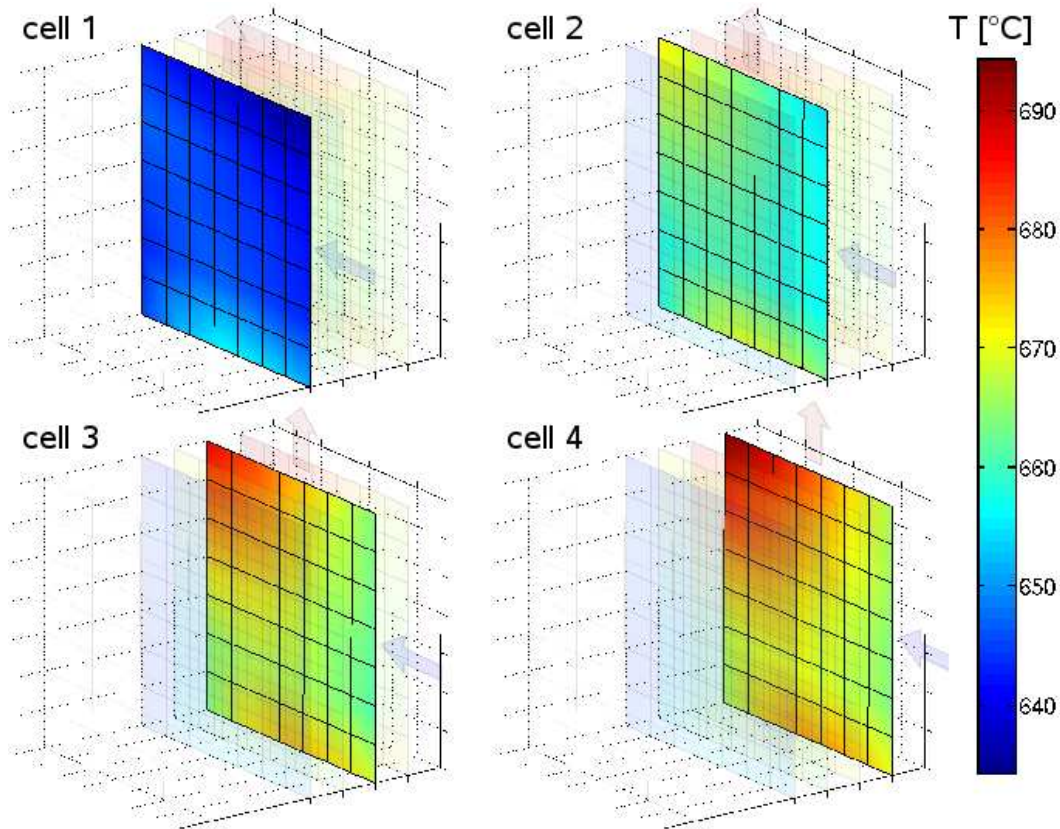


Figure 5: Temperature profile within the solid phases of the four fuel cells. The reforming unit (IIR), where the endothermic reforming reaction takes place, is located on the right hand side of the first cell. The flow direction within the anode and cathode gas compartments are indicated by the arrows.

645°C (cell 1) or 660°C (cell 2). On the other hand, the fuel cells located farer away from the IIR feature a hot spot in the top left corner. Within these cells, a temperature difference of up to 30°C can be found.

5. Conclusions

The symmetric stack model allows the simulation of the axial stack temperature. The simulation results show a parabolic temperature profile between two reforming units. For the fuel cells, two different operating conditions could be identified, which mainly depend on the distance of the fuel cell to the next reforming unit. Due to the endothermic methane reforming reaction in the IIR the temperature profile within the neighboring fuel cell is cooled down and unified while the other fuel cells are less affected. This shows that not only the temperature profile within a single cell is of importance for the design of an MCFC. In fact, the temperature profiles within a whole symmetric stack unit have to be considered to ensure an efficient and safe operation of these systems. The presented stack model is a suitable tool for this purpose.

6. References

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