A Partial Differential Algebraic Dynamic Model of a Molten Carbonate Fuel Cell

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Fuel cells convert chemical energy of hydrogen directly into electrical energy providing a clean and highly efficient source of electricity. In this paper we present a partial differential algebraic equation model that describes the gas flow, temperature and electrical potential depending on the reaction kinetics in a molten carbonate fuel cell. Furthermore we will present results for the numerical simulation of this time dependent two dimensional model.

1 Functionality of a Fuel Cell

A fuel cell consists of anode and cathode gas channels that are separated by electrolytes. Activated by a catalyst, hydrogen in each anode is converted into protons and electrons. The electrons go through an external circuit, creating a flow of electricity. The protons move through the electrolyte to the cathode, where they combine with the oxygen. Our model is based on a molten carbonate fuel cell that uses a molten carbonate salt as electrolyte and produces the necessary hydrogen from natural gas (methane) by an internal reforming reaction [1].

2 Model Description

The gas concentrations of seven involved substances (methane, hydrogen, water, oxygen, carbon monoxide, carbon dioxide, nitrogen), the molar flows, the temperatures and the electrical potentials in the anode and the cathode can be described by a system of partial differential algebraic equations depending on time \( t \) and two space dimensions \( (z_1, z_2) \). The fuel cell works in a cross flow. The anode gas flows in \( z_1 \) direction and the cathode gas in \( z_2 \) direction. The following transport equations describe the cross flow of the gases, whereas \( x_{a,j} \) for \( j = 1, \ldots, 7 \) denote the gas concentrations of the different substances, and \( \theta_a \) the temperature in the anode. Analogously \( x_{c,j} \) for \( j = 1, \ldots, 7 \) are the gas concentration and \( \theta_c \) the temperature in the cathode. The terms \( \phi_{1,j}, \phi_{2,j} \) for \( j = 1, \ldots, 7 \) and \( \phi_3, \phi_4 \) include the effects of the chemical reactions on the concentrations and temperatures.

\[
\frac{\partial x_{a,j}}{\partial t} = -g_a \theta_a \frac{\partial x_{a,j}}{\partial z_1} + \phi_{1,j}(\theta_a, \theta_a, x_a, \Phi_a), \quad \frac{\partial x_{c,j}}{\partial t} = g_c \theta_c \frac{\partial x_{c,j}}{\partial z_2} + \phi_{2,j}(\theta_c, \theta_c, x_c, \Phi_c), \quad j = 1, \ldots, 7,
\]

\[
\frac{\partial \theta_a}{\partial t} = -g_a \theta_a \frac{\partial \theta_a}{\partial z_1} + \phi_3(\theta_a, \theta_a, x_a, \Phi_a), \quad \frac{\partial \theta_c}{\partial t} = g_c \theta_c \frac{\partial \theta_c}{\partial z_2} + \phi_4(\theta_c, \theta_c, x_c, \Phi_c).
\]

The following degenerated PDEs specify the transport of molar flow in the anode \( g_a \) and cathode \( g_c \) including terms of the reaction kinetics \( \phi_5, \phi_6 \).

\[
0 = \frac{\partial (g_a \theta_a)}{\partial z_1} + \phi_5(\theta_a, \theta_a, x_a, \Phi_a), \quad 0 = \frac{\partial (g_c \theta_c)}{\partial z_2} + \phi_6(\theta_c, \theta_c, x_c, \Phi_c).
\]

Furthermore, a heat equation for the temperature \( \theta_a \) in the solid phases of the fuel cell is used. The function \( \phi_7 \) describes the heat exchange between solid and gas phases and the heat induction by the electrochemical reactions or the ion transport.

\[
\frac{\partial \theta_a}{\partial t} = \lambda \Delta \theta_a + \phi_7(\theta_a, \theta_a, \theta_c, x_a, x_c, \Phi_a, \Phi_c, \Phi_e, \Phi_v).
\]

Additionally the electrical potentials \( \Phi_a, \Phi_c, \Phi_e \) and \( \Phi_v \) of the anode, cathode, electrolyte and the whole cell are modeled by additional differential equations depending on the current density \( i \),

\[
\frac{\partial \Phi_a}{\partial t} = (i - i_a(x_a, \theta_a, \Phi_a, \Phi_e))/c_a, \quad \frac{\partial \Phi_c}{\partial t} = -(i - i_c(x_c, \theta_c, \Phi_a, \Phi_c, \Phi_e))/c_e,
\]

\[
\frac{\partial \Phi_e}{\partial t} = -(i - i_e(x_e, x_c, x_a, \theta_a, \Phi_a, \Phi_c, \Phi_e))/c_e, \quad \frac{\partial \Phi_v}{\partial t} = -\left( \int_0^1 \frac{1}{I_{cell}} dz - I_{cell} \right) / c_v.
\]

The current density \( i \) is determined by the algebraic equation

\[-\Phi_a(t, z) + \Phi_c(t, z) + \Phi_e(t, z) + \Phi_v(t) = 0.\]

Summarizing we have a system of 23 differential equations of mixed hyperbolic and parabolic type including partial differential equations and an algebraic equation. Suitable initial and boundary conditions are to be chosen.
3 Numerical Results

To solve this partial differential algebraic equation system numerically we have developed a specially tailored solver. We use implicit time integration, the heat equation is approximated by finite differences. For the transport equations we use upwind differences. Furthermore we take advantage of the three different time constants of the variables and solve the system of equation implicitly in time for variables that are slower in time.

The electrical potentials run very fast into the steady state. Thus in the first block we solve the equations for the potential and approximate the slower gas concentrations and temperatures by variables of the last time step. In the second block we solve the equation system for the gas concentrations and temperatures in the anode and the cathode channel using the just calculated potentials and the ‘old’ solid temperature. In the third and last block we can solve the slow solid temperature using the already calculated results.

The first figures show the results for the numerical simulation of the fuel cells in the anode (only one representing time step). The gas inlet of the fuel cell is at $z_1 = 0$ and we have a flow in $z_1$ direction. In the first picture we see methane with a high methane inlet and a methane consumption inside of the channel due to the reforming reaction. In the second picture we see hydrogen with a small amount at the inlet and then an increase because of the methane consuming, but hydrogen producing reforming reaction. At a certain level of hydrogen the electron producing reaction starts and hydrogen is consumed. The supplied gas is hot. Therefore the temperature at the anode inlet is high, see the third picture. Because of the endothermic reforming reaction the temperature starts to decrease, but increases as the exothermic electron releasing reaction makes an impact.

Fig. 1 Methane, hydrogen and temperature in anode channel

The next figures show the results for the cathode. The gas inlet of the fuel cell is now at $z_2 = 0$ and the gas flows in direction $z_2$. The first and second picture show the increasing of water and the decreasing of carbon dioxide due to the reactions in the cathode. This reaction is endothermic, so the cathode temperature is decreasing.

Fig. 2 Water, carbon dioxide and temperature in cathode channel

Additionally the temperatures of anode and cathode are linked by the heat conduction to the solid. Due to the cross flow of the gases the anode temperature is not uniformly distributed in direction $z_2$ and the cathode temperature not in $z_1$ direction. These temperature differences in the channels effect the reactions rates. Thus, with a higher anode temperature, e.g., at $z_2 = 1$ than at $z_2 = 0$, we have a higher reaction rate of the hydrogen consuming and free electrons releasing reaction in the anode.

By means of these results we are able to predict the behavior of the plug flow and temperature in the fuel cell. This allows an observation of the temperature gradients in the cell in order to reduce material wear and to increase efficiency. This a first step towards an optimization of the operation of molten carbonate fuel cells.

References