Comparative analysis of time constants in Solid Oxide Fuel Cell processes – selection of key processes for modeling power systems

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Abstract

The article presents a comparative analysis of the time constants of the main processes in the SOFC. The analysis was used to determine those processes most relevant to the modeling of an energy system comprising a fuel cell. The hybrid system, in addition to the fuel cell, has other devices (such as compressors, turbines, heat exchangers, etc.) working with it that may limit permissible ranges of parameter changes during transient processes. On the other hand, fuel cells affect other devices making up the system, including by restricting their operation in terms of dynamic responses.

Determination of time constants of the main processes in the cell and their analysis and comparison with time constants of other devices will allow selection of the most important processes from modeling point of vies and simplify the dynamic fuel cell model, so the class of fuel cell will match classes of models of other system elements.

Keywords: dynamic modeling, Solid Oxide Fuel Cell

1. Introduction

Rising fuel prices alongside increased consumption of electricity will provide a strong stimulus to engineer substantially, more efficient systems for power generation, than are currently in service. Fuel cells convert the chemical energy of fuel directly into electricity through electrochemical processes, so they are not limited by maximum cycle thermal efficiency. In addition, high-temperature fuel cells can be used as a heat source for traditional thermal cycles, thereby creating hybrid systems with a potential for ultra-high efficiency (70%). Currently, dynamic models of individual components of the power plants are based mainly on zero-dimensional models, where in addition to the static characteristics of the equipment, the corresponding dynamic characteristics are taken into account (accumulation of heat and matter, rotating inertia, etc.)

In order to choose an optimal control system and the operation parameters of both fuel cells and the elements cooperating with them, a suitable dynamic model of SOFC cells congruent with other components of the system is needed.

In the available literature there are few well-developed dynamic SOFC models, the authors mainly focus on modeling the cell in the changed conditions based on the current-voltage curves obtained from previous experiments. Appropriate models of dynamic SOFC fuel cells are crucial to determining the time-dependent working parameters of

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these objects and possible cell destruction resulting from overly rapid changes in load (thermal stress), or from life-cycles (cyclical changes in load.)

Research on modeling the dynamics of SOFC fuel cells is currently ongoing in several research centers in the world. Only fragmentary information can be found in the available literature and the presented data are often, given the lack of material information [1–6], rather unusual mathematical models of the fuel cells are used [1, 5–7], or no description of the models used is presented at all [1, 3, 4, 8]. Approximation algorithms were used for modeling the fuel cell behavior, in dynamic mode . Analysis of the dynamics of cells solely based on the purely electric approach (times are analyzed in-seconds) is also found [7, 9]. Some authors restrict themselves to only a description of the principles of conservation of mass and energy equations used during modeling [10]. There are data sets collected from different sources [11] as well as the experimental data for the start-up and shut-down of the fuel cell unit [8]. Dynamic operation is also associated with control issues [8]. The most advanced work can be found in [12] and [7], where some time constants of the fuel cell processes were given.

Often, a fuel cell is a part of larger system containing other devices. The most advanced configurations are called hybrid and involve the fuel cell cooperating with a gas-turbine subsystem. Thus, additional analyses are made in light of the dynamics of the fuel cell and other system elements (turbine, compressor, heat exchangers, etc.) to determine what the main constraints on the system during load changes. From the perspective of the entire system, a fuel cell is mainly a heat and mass accumulator and to a certain extent its function is similar to that of a heat exchanger. Therefore, different procedures should be used during start-up of the system and the other during normal load changes. In the case of start-up, the key elements may be devices with moving parts – air compressor, gas turbine, pumps, etc. It is important for the fuel cell to have a controlled process of heating up to the operating temperature. Then, the manner in which the fuel cell collaborates with other elements of the system must be changed; from heating mode to cooling mode.

Electrical processes take place in an almost infinitesimally short period of time, in stark contrast to thermal processes, which may last a relatively long time. This impacts other aspects of cell operation in terms of start-up procedures and operation during normal load changes. The main restrictions on fuel cells operation involve issues relating to the balance of the heat stack to cope with rapid load changes. These data are compared against each other and key processes are determined with regard to the dynamics.

Start-up procedures and load change procedures are proposed, these being dependent on system configuration and fuel cell stack design.

In lumped system analysis, time constant (τ) is used for identification of processes which are proceeded uniformly with time. Physically, the time constant defines when the system reaches the value of (1-1/e) of its final (often asymptotic) value for the analyzed parameter. The value of (1-1/e) is equal to about 63% of the final result. For very simple cases such as linear models the time constant can be derived from differential equation, e.g.:

$$\frac{dX}{dt} + \frac{1}{\tau}X = f(t) \tag{1}$$

where: X – analyzed variable, τ – time constant.

In other cases, the time constant should be obtained based on adequate dynamic simulation of the system or measured values from experimental investigations.

2. Comparative analysis of time constants in processes of the Solid Oxide Fuel Cell

Fuel cells including SOFCs are devices which produce direct current through electrochemical processes. This is achieved by delivering working fluids into two fuel cell sides: anode and cathode. In addition to electrochemical processes, there are also mass flows, chemical reactions, composition changes, heat exchange and other phenomena. All those processes are characterized by various time constants. The main processes are divided into the following groups:

- Electrical processes (e.g. electric current flow)

- Electrochemical processes (e.g. electrons capture by oxygen)

- Chemical processes (e.g. reforming reactions)

- Flow (working fluid flow across fuel cell channel)

- Compositions (e.g. mixing two flows)

- Diffusion (e.g. reaction subtracts and products mixing)

- Thermal processes (e.g. heat generation, heat losses)

Electrical processes are mainly associated with all electric equipment of SOFCs, including current collector meshes, wires, and DC/AC converters. The time needed to achieve steady-state conditions is a matter of micro seconds. Usually, those processes occur independently (e.g. of temperature).

Electrochemical processes are preceded on both fuel cell sides, at the cathode side two electrons are captured by an oxygen atom to form an oxygen ion (O^{2-}). At the anode side, the reverse process occurs with the oxygen releasing two electrons to an external circuit and then reacting with the fuel (e.g. hydrogen). All those processes occur on the triple phase boundary (TPB) where gaseous fluid must simultaneously meet electrons and the solid part of the electrolyte. Thus, time constants are determined by the active area of the fuel cell, electrode thicknesses and porosities, among others. Usually, at elevated temperatures the electrochemical processes are relatively rapid, with time constants ranging from 0.08 to 0.18 s.

Chemical processes involve reactions which occur during fuel cell operation. Those processes are strictly dependent on temperature and the catalyst used. Kinetic theory should be applied to estimate the time constants. If no catalyst is used nor activation energy delivered, the time constant of various reactions vary over a wide range. For instance, at 800°C, hydrogen reacts with oxygen in 0.04 s, whereas methane reacting with oxygen must have about 2.5 thousands years to achieve chemical equilibrium.

Fluid velocities across the fuel cell channel are relatively slow. At the laboratory scale, both fuel and oxygen flow velocities are in the range of 0.5–3 m/s. This means that, assuming fuel cell channel length
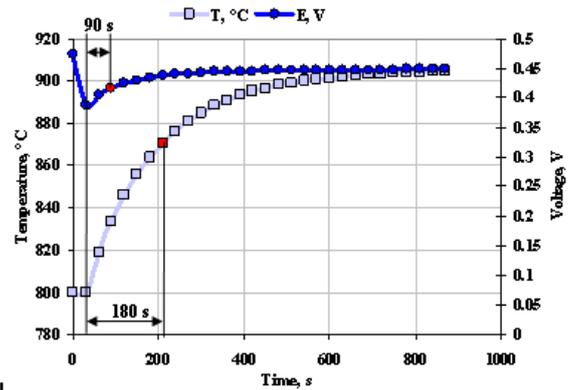

Figure 1: Time response of singular solid oxide fuel cell mounted between two manifolds. Red dots indicate adequate time constants for voltage and temperature

of 4 cm, the working fluid is present in the fuel cell for an estimated 1 s. A large fuel cell area together with low fluid velocities result in high accumulation volumes.

Diffusion is heavily dependent on temperature and the diffusion coefficient value. In the case of material porosity, other aspects play an important role (pore diameter) and diffusion models other than Fick or Stefan-Maxwell must be taken into consideration (Knudsen diffusion). At elevated temperatures (e.g. 800°C) diffusion processes are very rapid (below 1 s for H_2/H_2O) and the related time constant is also very short.

Thermal processes are correlated with several diverse aspects. The first is the heat generated during fuel cell operation as a function of internal resistances of the electrolyte. Heat is generated proportionally to the electric current drawn. The reactions taking place inside the fuel cell channel can be endothermic or exothermic. This means that heat can be either generated or consumed. Additionally, there are two cell cooling possibilities; the first is by an air flow delivered to the cathode channel and the second is by heat losses to the surroundings by radiation or convection. Time constants of temperature response are then dependent on both architecture and material aspects. The singular plate of the SOFC represents less than 20% of total fuel cell stack, while the main thermal capacity is provided by the manifolds, collector and housing. The time constants related to the solid parts are very long (more than 100 s); additionally, temperature determines other parameters, e.g.

cell voltage. An example of this behavior is given in Fig. 1, where it can be seen that the long response in temperature results in a relatively long time constant for voltage. The figure presents the changes in temperature and voltage from increasing fuel cell current density by 20% without control system intervention. It can be seen that voltage reaches a value of (1-1/e) of its asymptotic result in a period of less than 90 s, whereas the temperature response is longer, with an adequate time constant of 200 s. Compositions are altered by electrochemical reactions occurring on fuel cell surfaces and chemical reactions occurring inside fuel cell channels. Both electrochemical and chemical reactions are influenced by diffusion, which is responsible for transporting the reaction products and subtracts. Most of the reactions occur on the at anode side of the fuel cell where oxygen ions react with a fuel and steam reforming of methane occurs itself. In sum, the time constants of the composition changes are correlated with all those types of processes (as explained earlier).

3. Discussion and conclusions

SOFC construction is very similar to the construction of a heat exchanger (large areas, two working fluids, solids parts, no moving parts, etc.). On the other hand some processes are almost instantaneous (e.g. current, diffusion, specific chemical reactions).

From the dynamic point of view, an SOFC can accumulate large amounts of heat and mass, together with long response times (large time constant) the introduction of an SOFC into a gas turbine subsystem greatly changes the working of the whole system. Even rapid changes in current and voltage values (SOFC power) have a long time influence on the gas turbine subsystem which must keep the SOFC in safe operation mode.

The collaboration of the SOFC with a gas turbine may result in over-control of GT; even if the fuel delivered to the combustion chamber is cut, the heat accumulated in the fuel cell will still keep turbine inlet temperature increased. In an ordinary system, this issue is solved by by-passing the heat accumulating device – which would be seems to be difficult with a SOFC because the stack must be cooled continuously. It seems that proper control of the hybrid

can be delivered through using an electric generator to varying the system is varying the gas turbine rotational speed.

The most important processes in modeling systems which contain fuel cells are thermal processes, due to their influence on the other parameters which are separately much faster (e.g. voltage). A secondary order is accorded to chemical reactions, which while very difficult to model (kinetic and catalytic behavior) may strongly influence both thermal and electrochemical processes. In general, it often assumed that only one reaction occurs on fuel cell surfaces i.e. hydrogen oxidization, but this assumption seems to provide only very rough estimations of fuel cell performances.

Other processes, such as electric, electrochemical, diffusion, and pressure changes, can be assumed as time-independent and modeled in steady-state conditions. Only if strictly electrical behavior requires investigation (time constant at about 1 μs) do those processes needed to be modeled in relation to time.

From the analysis presented herein it can be concluded that, from the dynamic point of view, a solid oxide fuel cell behaves in a similar way to a heat exchanger. Among other things, both have comparable time constants (longer than 100 s).

The most important processes according to the model of dynamic operation of a hybrid system are: thermal behavior of solid parts and heat accumulation relative to them. Mass accumulation is also a very important issue to take into consideration.

Fuel is used in a similar way by SOFC and combustion chamber utilize alike – by oxidization. But the activation energy in combustion chamber is delivered by fire, whereas an SOFC the reaction takes place partly on the cathode side and partly on the anode side. There is no way to deliver activation energy and only one solution can be applied – a catalyst. Therefore, the reaction type, the temperature and the catalyst layer impact greatly on the total response of the fuel cell. This complicates any dynamic model of the system by requiring the factoring in of chemical reaction kinetics.

The delay in response accorded to clear electric processes can be disregarded.

Table 1: Time constants of the main processes

SOFC		Other system elements	
Electrochemistry	0.08–0.18 s	Ejector	0.04 s
Voltage change	60 s	Fuel combustion	< 1 s
Electric capacity	< 1 s	Valve	1 s
Diffusion	< 1 s	Turbine	< 10 s
Current change	< 1 s	Compressor	< 90 s
Heat capacity of solid parts	> 100 s	Heat exchanger	> 100 s
Singular fuel cell plate with two manifolds	200 s		
Reactions	Time constant	Chemical equilibrium time	
H_2+O_2 reaction at 800°C	10^{-7} s	0.05 s	
$CO+O_2$ reaction at 800°C	$2 \cdot 10^{-5}$ s	0.5 s	
CH_4+O_2 reaction at 800°C	0.9 s	3 150 years	

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