

# THE MAIN RELATIONSHIPS OF THE MAIN PARAMETERS OF THE PROTON CONDUCTING SOFC

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## ABSTRACT

The main relationships required for describing phenomena occur in proton conducting Solid Oxide Fuel Cells are presented. The relationships are segregated according their influence on the specific fuel cell features. A sensitivity analysis of the chosen parameters and validation against the experimental data are presented. One missing relationship is identified: electronic conductivity of proton conductivity of solid electrolyte. Future activities are proposed.

**Keywords:** thermodynamic; chemical; physical and electrochemical parameters modeling

## NOMENCLATURE

$\epsilon$	porosity
$A$	fuel cell area, pre-exponential factor
$d$	characteristic size of the channel
$D_p$	pore diameter
$E_{act}$	activation energy
$F$	Faraday constant
$f$	friction factor
$i$	current density
$j$	number of layers in a fuel cell
$L$	channel length
$N$	molar flow of the reagent
$p$	partial pressure
$P$	contact pressure
$R$	ideal gas constant
$r$	specific resistance
$Re$	Reynolds number
$T$	temperature
$v$	gas velocity
$\delta$	thickness
$H$	contact surface roughness, utilization factor
$\rho$	fluid density, bulk resistivity
$\sigma$	material yield strength, conductivity

## 1. INTRODUCTION

Fuel cells, in particular high temperature Solid Oxide Fuel Cells (SOFC), are considered the most promising sources of electricity in the future. This is related to their potentially very high efficiency resulting from the direct conversion of fuel chemical energy into electricity, without using the heat cycle.

This work seeks to provide the base relationships for the main phenomena occurring during the operation of proton conducting SOFC. We pulled together all the relationships used for describing the processes, including chemistry, electrochemistry, mass transport and heat exchange among others. Where possible, we provided related experimental data and empirical factors. The theoretical background is given for all the relationships mentioned above. This provides added value for all researchers wishing to model the H+SOFC and the knowledge can be upgraded when new information becomes available.

In previous work we identified key parameters of H+SOFC, as set out in Table 1. Most of them were identified experimentally and their ranges are given. Flow parameters can be factored in by applying flow equations and the thermodynamic function of the fluid used. The most difficult ones to determine are contact resistances (both thermal and electrical) and inter-layer phenomena. Impedance spectroscopy is one possible tool to identify them, but data is scarce.

We did not find any data concerning the pure electric conductivity of the proton-conducting electrolytes. This may mean that conductivity does not exist at all or that its influence can be neglected. We will pay special attention to this in future work.

Table 1: Key parameters of H+SOFC from the model viewpoint

Key parameter	Range
Temperature, °C	600 .. 1000
Protonic conductivity, S/cm	0.001 .. 0.01
Electronic conductivity, S/cm	no data
Anode thickness, mm	0.25 .. 0.7
Cathode thickness, mm	0.5 .. 0.7
Electrolyte thickness, μm	5 .. 150
Anode porosity, wt. %	20 .. 50
Cathode porosity, %	40 .. 50
Contact pressure, bar	0.2 .. 0.9
Flow density, ml/cm <sup>2</sup> ,	8.05 .. 375

In this work, we focused on the main relationships that can be used to describe the influence of the selected parameters of proton conducting solid oxide fuel cells.

## 2. MAIN RELATIONSHIPS FOR MAIN PARAMETERS OF PROTON CONDUCTING SOFC

### 2.1 Maximum voltage—Nernst voltage

In order to determine the maximum work to be achieved in H+SOFC, the number of moles performing this work and the pressure ratio must be determined. The current generated in the fuel cell is linked to the number of protons passing through the electrolyte, which carries out the work. Using Faraday's law equation, the maximum fuel cell voltage can be derived:

$$E_{max} = \frac{R \cdot T}{2 \cdot F} \ln \frac{p_{H_2, anode}}{p_{H_2, cathode}} \quad (1)$$

Partial pressure of hydrogen on the anode side can be easily determined, as hydrogen is fed as a fuel. On the other hand, the partial pressure of hydrogen at the cathode is much more difficult to identify (and measure). Often we can use the chemical equilibrium constant (K), which is usually presented in the literature in the form where the denominator relates to the substrates and the numerator to the products of reaction. It should also be noted that the values of equilibrium constants depend on the notation of the reaction.

### 2.2 Utilization of reagents

The influence of reagent utilization factors on H+SOFC performance has multiple impacts. In similar fashion to the electric current, the flows can be referred to the active area of fuel cell. The anode flow delivers fuel to the fuel cell (hydrogen) and the cathode flow delivers oxidant (air). The flow content and its amount can be described by using a

utilization factor—the amount of reagent consumed by the fuel cell in relation to the amount delivered:

$$\eta = 1 - \frac{n_{out}}{n_{in}} \quad (2)$$

Where more complex compositions are fed to both sides of the fuel cell, the fuel utilization factor can be recalculated for the equivalent amount of reagent with consideration of the reactions which occur there. In fact, due to the presence of area specific electronic resistance, real fuel utilization will never reach a value of 0. It is more convenient to use the fuel utilization factor defined by the amount of electric current taken from the fuel cell, because its value can vary in the range 0 to 1, and the real value of  $\eta$  must be calculated iteratively.

### 2.3 Maximum current density

Current density is a fundamental parameter in fuel cell technology, correlating the amount of electric current taken from the fuel cell for a specific active area. The total current which can be drawn from the cell correlates strictly with the amount of either fuel or oxidant delivered. This means that it is a value of current for which the whole fuel is utilized— $I_{max}$ :

$$i_{max} = \frac{4F \cdot n_{O_2, equivalent}}{A} \quad (3)$$

In the case of proton conducting fuel cells fueled by hydrogen, insufficient oxidant is often delivered to the cathode side of the fuel cell, thus the maximum current (density) needs to be referred to this value.

### 2.4 Protonic conductivity

Proton-conducting materials constitute a class of oxide compounds possessing the required properties for application as electrolytes for low and intermediate temperature SOFCs [1-2]. However, ionic conduction is caused by both oxygen ion and proton transport with a prevailing character of the latter [3]. Two types of relationships can be found for describing specific proton conductivity of the electrolyte layer. According to [4] protonic conductivity can be calculated using the following formula:

$$\sigma_{ele} = A \cdot e^{-\frac{E_{act}}{R \cdot T}} \quad (5)$$

Factors A and  $E_{act}$  for formula (5) were determined from the experimental data available in the literature (see Fig. 1). In [7], it was also noticed that protonic conductivity is highly dependent on temperature:

$$\sigma_{ele} \cdot T = A \cdot e^{-\frac{E_{act}}{RT}} \quad (6)$$

Electrodes of proton conducting SOFCs can contain a mixture of proton conductors and electron conductors [8-10]. The total area specified internal resistance is not easy to estimate. Additionally, electrodes comprise a porous layer (multi-layer design is also possible). There is no reason not to use the same equation as for protonic conductivity Eq. (5). In [11], we can see how porosity [12-13] is included in the equation by linear approximation:

$$r_j = \frac{\delta_j \cdot (1 - \epsilon_j)}{\sigma_j} \quad (7)$$

### 2.5 Electronic/Electron conductivity

In general, materials used for the electrolyte layer are assumed to be only proton conductors, but in fact electron conductivity can be present in similar fashion to oxygen ion conducting solid oxide fuel cells [14]. On the other hand, hydrogen leakage through the electrolyte has the same effect as electron (electrical) conductance and can be described in the same way.

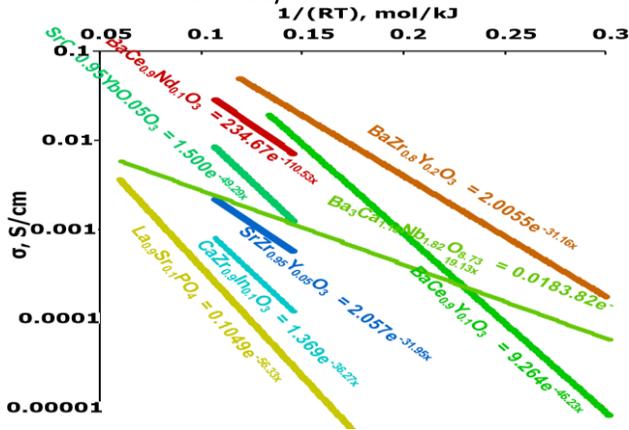


Figure 1: Proton conducting materials used as electrolytes in H+SOFC [5-6]

The second type of internal resistance is electrical resistance— $r_2$ . The influences of temperature and electrolyte thickness on the electronic internal resistance of electrolytes are not well known. The electronic conductivity values of proton conducting electrolytes are spread across a very wide range. They do not have a major impact on calculated cell voltage for high current densities. It is hard to measure the electronic resistance of proton conducting electrolytes, since they have both protonic and electronic conductivities simultaneously, giving total electrical resistance. It should be noted that decreasing electrolyte thickness reduces protonic resistance (positive effect), but probably reduces electronic resistance (negative effect) as well. The value of electronic resistance of the cell can be estimated from

available experimental results by using an equation that describes a proton conducting SOFC voltage and substituting  $\eta = 0$ . The resistance can also be estimated by using electrochemical impedance spectra [15], this issue will be investigated by us in detail shortly.

### 2.6 Partial pressures in the reaction zone

As the Nernst equation is often based on partial pressures of main reagents, estimation of these pressures is crucial when calculating fuel cell performance. There are many methods for modeling transport inside electrodes [16]. In more advanced studies a fully three dimensional, multiphase, micro-scale solid oxide fuel cell anode transport phenomena numerical model is used. The Butler-Volmer model is combined with empirical relations for conductivity and diffusivity—notably the Fuller Shetler-Giddings equation and the Fickian model for transport of gas reagents.

Main reactions occur at the cathode, where hydrogen is released from the electrolyte layers and reacts with oxygen. The partial pressures of the reagents can be calculated by using a utilization factor and chemical equilibrium constant for hydrogen/oxygen reaction. Non-equilibrium conditions can appear when reactions are very slow, and there is no time/space to reach the chemical equilibrium state. The phenomena are described by the reaction rate, what is strongly dependent on the reaction temperature. On the other hand, there are reactions other than utilization of hydrogen at the cathode, like solid/gas interface where hydrogen is captured and split into protons and electrons.

Electrodes are made as porous layers with the porosity factor in the range of 0.5 to 0.8. Through the anode, the hydrogen flows in the direction of the electrolyte, whereas at the cathode there are two flows in counter directions: oxygen to electrolyte layer and water from electrolyte layer. Those flows influence the partial pressures of reagents (hydrogen at the anode; oxygen and water at the cathode). The pressure drop through the porous layer can be described by the Ergun equation, which was modified in [17]:

$$\Delta p = 2 \cdot f \frac{L}{d} \rho \cdot v^2 \quad (8)$$

$$f = \frac{550.7}{Re} + 14.5 \quad (9)$$

$$Re = \frac{\rho \cdot v \cdot D_p}{\mu(1 - \epsilon)} \quad (10)$$

### 2.7 Contact resistance/pressure force

Contact resistance is a function of compressing force applied to the fuel cell sandwich, temperature, material yield and the contact area. The two parameters are not totally independent: by increasing pressing force, the contact area also improves. There are a few ways to describe the phenomena [18] and they can be combined in the following equation:

$$R_{contact} = (\rho_1 + \rho_2) \left[ \frac{1}{4} \left( \frac{\pi \sigma_{YS}}{\eta P} \right)^{\frac{1}{2}} + \frac{3\pi}{15\eta^{\frac{1}{2}}} \right] \quad (11)$$

### 3. CONCLUSIONS

The main relationships of the main parameters of proton conducting SOFCs are collected and described. Temperature influences the maximum voltage directly through the Nernst equation and indirectly through diffusion coefficients, which determine partial pressures at the reaction place. Protonic conductivity is also a strong function of temperature. Electrolyte, anode and cathode thicknesses are taken into account by the conductivity equation and have linear influences. Anode and cathode porosities change the maximum voltage equation (influencing partial pressures of reagents by Ergun relationships), they also determine the active area exposed to gases, and finally the contact resistance by defining rough of the contacting surface. The contact resistance is also strongly influenced by the pressing force applied to the cell. The novelty of this paper is that the relationship and experimental data for the electric resistance of proton conductors were not found, thus necessitating further experiments.

The paper brings together the relationships which describe the main parameters from the viewpoint of mathematical modeling of proton conducting SOFCs. The next step will be to construct a model based on the reduced order approach [19-20].

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