

PEDRO NEHTER

THEORETICAL  
ANALYSIS OF HIGH  
FUEL UTILIZING  
SOLID OXIDE  
FUEL CELLS

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## PREFACE

The commercialization of fuel cells needs further developments in materials, power density and durability. These key issues are strongly related to the choice of electrochemical, thermodynamic and design parameters. This applies in particular to the sensitivity of the solid oxide fuel cell's (SOFC's) power density and durability. Achieving high power density has to be assessed carefully with regard to the cell's voltage, fuel utilization and efficiency.

The operation at high fuel utilization is particularly critical due to the decrement in the Nernst voltage and the formation of nickel oxide at nickel cermet anodes. Both effects are influenced by the local hydrogen to water ratio of the anode gas. Therefore, it is essential to understand the local resolution of the gas composition and its influence on the total power density. In this context, analytical solutions of the integral current density at a constant area specific resistance (ASR) are presented in this study.

As a result of the transferred species, loss mechanisms occur. These polarization losses are sensitively influenced by numerous mechanisms, which are strongly non-linear. Therefore, a finite difference model is chosen to analyze the influence of the major operational parameters on the power density. It is based on a two dimensional resolution of the local energy balance in the axial and radial direction of a tubular SOFC. This model includes heat transfer by conduction, convection and radiation as well as the heat sources due to the chemical and electrochemical reactions. The shift reaction and the reforming of residual methane are taken into account by a kinetic approach. The electrochemical losses of the hydrogen oxidation are determined by commonly used Butler-Volmer equation, binary diffusion, Knudsen diffusion and ohmic law.

Based on the finite difference simulation, a novel conceptual solution is proposed which allows improvements in the fuel utilization and power density.

The proposed configuration consists of an anode gas condenser which is used to increase the fuel utilization from 85% to 94-97% at a constant total cell area and higher efficiency. In this context, the tendency of the formation of nickel oxide at the anode is approximately estimated to take roughly the durability of the anode into account. This system could be applied to stationary CO<sub>2</sub> sequestering applications. Using methane as fuel, it is further shown that the CO<sub>2</sub> can be separated with a minimum demand of energy with the high fuel utilizing SOFC gas turbine cycle.

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## Chapter 1

# INTRODUCTION

Previous studies have shown that solid oxide fuel cells (SOFC) promise highest system efficiencies [1,2]. This is mainly caused by the comparably low exergetic losses within the SOFC stack [3]. Siemens Westinghouse demonstrated the high durability of an atmospheric (system pressure  $\approx 1.3$  bar) SOFC system with a performance of 100 kW. The efficiency of such atmospheric SOFC systems mainly depends on the average cell voltage, the electrochemical fuel utilization and the demand of excess air. The fuel utilization is commonly chosen with 85% at Ni-Cermet anodes. A further amount in fuel utilization would result in a stronger formation of nickel oxide, which decreases the catalytic activity for the hydrogen oxidation. This effect is partly reversible but has to be avoided to increase availability and durability. To achieve appropriate system efficiencies, highest fuel utilizations are aspired in particular for SOFC systems which are not coupled with heat engines. In this context, it is necessary to consider the limitation mechanisms in fuel utilization with respect to the cell's power density and degradation mechanisms.

## NOMENCLATURE

$a$	$[\text{m}^2 \text{s}^{-1}] / -$	thermal conductivity coefficient / activity
$A$	$[\text{m}^2]$	Area
$ASR$	$[\Omega \text{m}^2]$	area specific resistance
$c_p$	$[\text{kJ mol}^{-1} \text{K}^{-1}]$	heat capacity
$C$	$[\text{W m}^{-2} \text{K}^{-4}]$	radiation exchange factor
$d$	$[\text{m}]$	diameter
$D$	$[\text{m}^2 \text{s}^{-1}]$	diffusion coefficient



## NOMENCLATURE (CONTINUED)

$E_N$	[V]	Nernst voltage
$F$	[As mol <sup>-1</sup> ]	Faraday constant
$G$	[kJ mol <sup>-1</sup> ]	Gibbs free energy
$GT$		gas turbine
$H$	[kJ mol <sup>-1</sup> ]	enthalpy
$i$	[Am <sup>-2</sup> ]	electrical current density
$\bar{i}_{total}$	[Am <sup>-2</sup> ]	average electrical current density
$I$	[A]	electrical current
$j_0$	[A m <sup>-2</sup> ]	exchange current density
$k$	[mol/m <sup>2</sup> bar <sup>2</sup> s] / [J/K]	reaction rate coefficient / Boltzmann constant
$K_p$	-	equilibrium constant
$M$	[g mol <sup>-1</sup> ]	molar mass
$Ni$		nickel
$\dot{n}$	[mol s <sup>-1</sup> ]	molar flow
$P$	[W]	power
$p_{el}$	[Wm <sup>-2</sup> ]	area specific power
$p$	[bar]	partial pressure
$\dot{q}$	[W m <sup>-3</sup> ]	volumetric heat source
$r$	[m]	radius
$R$	[kJ mol <sup>-1</sup> K <sup>-1</sup> ] / [ $\Omega$ ]	universal gas constant / ohmic resistance
$SOFC$		solid oxide fuel cell
$S$	[J mol <sup>-1</sup> K <sup>-1</sup> ]	entropy
$S/C$	-	steam/carbon ratio
$T$	[K]	absolute temperature
$u_f$	-	fuel utilization
$V$	[V]	voltage
$x$	-	molar fraction
$z$	[m]	axial length

## GREEK LETTERS

$\alpha$	[W m <sup>-2</sup> K <sup>-1</sup> ] / -	heat transfer coefficient / transfer coefficient
$\delta$	[m]	layer thickness
$\eta$	-	efficiency
$\hat{\eta}$	[V]	polarization
$\vartheta$	[°C]	temperature
$\bar{v}_A$	[m s <sup>-1</sup> ]	average velocity of the gas molecule
$\nu_i$	-	stoichiometric factor of component

## GREEK LETTERS (CONTINUED)

$\Delta \nu$	-	stoichiometric difference of reaction
$\rho$	[kg m <sup>-3</sup> ]	density
$\tau$	[s]	time
$\Omega_D$	-	the collision integral

## SUBSCRIPTS

Act	activation
Diff	diffusion
el	electrical
Elt	electrolyte
H <sub>2</sub>	hydrogen
H <sub>2</sub> O	water
i	component
irr	irreversible
Ca	cathode
Kn	Knudsen diffusion
loss	losses
O <sub>2</sub>	oxygen
Pol	polarization
rad	radiation
reac	reaction
Ref	reforming reaction
rev	reversible
shift	shift reaction
Sys	system



## Chapter 2

# ANALYTICAL SOLUTION OF THE CURRENT DISTRIBUTION

## 2.1. POWER DENSITY

The total power  $P_{el}$  of a single cell with an equipotential cell area is given by the integral of the differential power.

$$P_{el} = V_{Cell} \cdot \int dI \quad (1)$$

The area specific power density  $p_{el}$  is a common parameter which is used to estimate the required cell area at a specific total power. It is determined by the quotient of the total power and the total cell area  $A$ , whereas the quotient of the total current  $I_{total}$  and the total cell area, which is calculated by the integral of differential currents  $dI$ , is equal to the average current density  $\bar{i}_{total}$ .

$$p_{el} = \frac{P_{el}}{A} = \frac{V_{Cell} \cdot \int dI}{A} = V_{Cell} \cdot \bar{i}_{total} \quad (2)$$

To solve this equation, it is necessary to consider the relation between the electrochemical conversion of the reacting species and the cell voltage. The electrochemical conversion of the reacting species in fuel cells is coupled directly with the exchanged electrical current. The molar consumption of reactants is determined by the Faradays law

$$\dot{n}_{H_2}^0 - \dot{n}_{H_2} = \frac{I_{total}}{2 \cdot F} \quad \dot{n}_{H_2O} - \dot{n}_{H_2O}^0 = \frac{I_{total}}{2 \cdot F} \quad \dot{n}_{O_2}^0 - \dot{n}_{O_2} = \frac{I_{total}}{4 \cdot F} \quad (3)$$

where 2 mol electrons per mol hydrogen and 4 mol electrons per mol oxygen are exchanged. This implies that the electrolyte is free of electric leaks and the electrodes are free of any parallel reactions. The index “0” is used for the molar flow at the entry of the cell (Figure 1). The quotient of the converted hydrogen and the maximum convertible hydrogen is defined as fuel utilization  $uf$ .

$$uf = \frac{\Delta \dot{n}_{H_2}}{\dot{n}_{H_2}^0} = \frac{\dot{n}_{H_2}^0 - \dot{n}_{H_2}}{\dot{n}_{H_2}^0} \quad (4)$$

The maximum convertible hydrogen can also be expressed as maximum available electrical current  $I_{max}$ ,

$$I_{max} = F \cdot 2 \cdot \dot{n}_{H_2}^0 \quad (5)$$

$$I_{total} = uf \cdot I_{max} \quad (6)$$

whereas the total electrical current  $I_{total}$  of the whole cell area  $A$  is proportional to the converted part of the maximum available current  $I_{max}$ . It is further assumed that the electrical current flow is exclusively directed perpendicular to the cell's area. Thus, ohmic losses in the direction parallel to the electrodes are neglected.

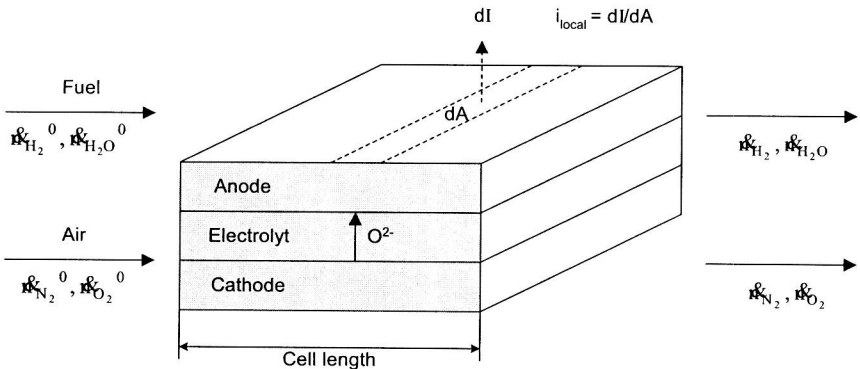


Figure 1. Schematic of a single solid oxide fuel cell.

In case of a non-linear distribution of the electrical current along the cell area, it is necessary to calculate the local current density  $i_{local}$ ,

$$i_{local} = \frac{dI}{dA} = \frac{I_{max} \cdot duf}{dA} \quad (7)$$

where the differential electrical current is equal to the differential utilization of the maximum current. In general, the existence of a current is caused by a potential gradient. In case of a fuel cell, the Nernst voltage  $E_N$  represents the driving force as potential gradient between the gaseous phases at the anode and the cathode. The Nernst voltage changes with the partial pressure of reacting species caused by the change in entropy. Thus, the influence of the fuel utilization on the Nernst voltage increases with higher operation temperatures.

$$E_{N,H_2} = -\frac{1}{2 \cdot F} \left[ \Delta^r G_{H_2(T)} + T \cdot R \cdot \ln \left( \frac{P_{H_2O}}{P_{H_2} \cdot \sqrt{P_{O_2}}} \cdot \sqrt{P_0} \right) \right] \quad (8)$$

As a result of the transferred species, loss mechanisms occur. These losses are well known as polarization losses in terms of the first law of thermodynamics. Polarization losses are sensitively influenced by numerous mechanisms which are strongly non-linear with respect to the operational parameters like the current density, electrical potentials, temperature, pressure, gas compositions and material properties. These parameters are assumed to be constant in case of a differential cell area, whereas the loss mechanisms are summarized in a constant area specific resistance ASR [ $\Omega\text{cm}^2$ ]. Thus, a change of the local overpotential ( $E_{N(uf)} - V_{Cell}$ ) at constant ASR complies with a proportional change in the local current density.

$$\frac{dI}{dA} = \frac{E_{N(uf)} - V_{Cell}}{ASR} \quad (9)$$

In general, high fuel utilizations are aspired to achieve high efficiencies, whereas different Nernst voltages occur along the cell area. Hence, the dependency of the fuel utilization from the electrical current (Eq. (7)) has to be implemented in Eq.(9).

$$\frac{I_{max} \cdot duf}{dA} = \frac{E_{N(uf)} - V_{Cell}}{ASR} \quad (10)$$

In this subsection, the ASR is assumed to be constant along the cell area to consider exclusively the influence of the Nernst voltage on the cell performance. Taking the local distribution of the current into account, this influence can be calculated by the integral of Eq. (10). This approach neglects the change in the Nernst potential caused by the diffusion in the gaseous bulk along the flow direction of reactants.

$$\int_{A=0}^{A=A_{total}} \frac{1}{ASR} dA = \int_{uf=0}^{uf=uf_{total}} \frac{I_{max}}{E_{N(uf)} - V_{Cell}} duf \quad (11)$$

Different conditions of SOFCs under test procedures and practical operation require different calculations for the evaluation of the test results. Thus, three cases at different distributions of the Nernst voltage are considered with regard to the solution of the integral cell area and integral fuel utilization, respectively.

Case A: Nernst voltage is constant

Case B: Nernst voltage changes inversely proportional with the fuel utilization

Case C: Nernst voltage changes according to Eq. (8)

The temperature of the gaseous phases and the SOFC are assumed to be equal and constant along the cell area.

#### Case A:

In case of comparably high maximum currents ( $I_{max} \gg I$ ), the gaseous outlet composition is similar to the inlet composition. Thus, the Nernst voltage along the isothermal fuel cell is approximately constant. This condition occurs mostly at material related characterization tests, whereas small cell areas are investigated.

$$\begin{aligned} p_{H_2,out} &\approx p_{H_2}^0 \\ p_{H_2O,out} &\approx p_{H_2O}^0 \end{aligned} \quad \rightarrow \quad E_N \approx const. \quad (12)$$

The solution of Eq. (11) at a constant Nernst voltage shows a linear dependency of the cell voltage from the overpotential, represented by the fraction term of Eq. (13). The Ohmic law is similar to this fraction term, where the voltage drop is proportional to the current density represented by the quotient of the utilized part of the maximum current and the cell area.

$$V_{Cell} = E_N - \frac{ASR \cdot uf \cdot I_{max}}{A} \quad (13)$$

The cell voltage governed by Eq. (13) and Eq. (2) gives the power density at a constant

$$p_{el} = \left( E_N - \frac{ASR \cdot uf \cdot I_{max}}{A} \right) \cdot \frac{uf \cdot I_{max}}{A} \quad (14)$$

#### Case B:

If the fuel utilization occurs in a range of hydrogen to water pressure ratios ( $p_{H_2}/p_{H_2O}$ ) between 0.7 and 0.3, the Nernst voltage changes approximately inversely proportional with the fuel utilization. Thus, a linear approach is used to determine the Nernst voltage from the fuel utilization,

$$E_{N(uf)} = E_N^0 + \frac{\Delta E_N}{\Delta uf} \cdot uf \quad (15)$$

where  $E_N^0$  is the Nernst voltage at the entry of the anode and  $\Delta E_N/\Delta uf$  is the slope of change in Nernst voltage.

$$\int_{A=0}^{A=A_{total}} \frac{1}{ASR} dA = \int_{uf=0}^{uf=uf_{total}} \frac{I_{max}}{E_N^0 + \frac{\Delta E_N}{\Delta uf} \cdot uf - V_{Cell}} duf \quad (16)$$

The solution for a linear Nernst voltage is given by



$$V_{Cell} = E_N^0 - \frac{\Delta E_N}{\Delta uf} \cdot uf \cdot \left[ \exp \left( \frac{\frac{\Delta E_N}{\Delta uf} \cdot A}{ASR \cdot I_{max}} \right) - 1 \right]^{-1} \quad (17)$$

and the power density is governed by

$$P_{el} = \left( E_N^0 - \frac{\Delta E_N}{\Delta uf} \cdot uf \cdot \left[ \exp \left( \frac{\frac{\Delta E_N}{\Delta uf} \cdot A}{ASR \cdot I_{max}} \right) - 1 \right]^{-1} \right) \cdot \frac{uf \cdot I_{max}}{A} \quad (18)$$

### Case C:

In practical applications, high fuel utilizations result in low of hydrogen to water pressure ratios at the outlet of the anode, whereas high hydrogen pressures occur at the entry of the anode. Thus, the non-linear dependency of the Nernst voltage from the fuel utilization has to be taken into account with respect to the integral solution of Eq.(11).

$$\int_{A=0}^{A=A_{total}} \frac{1}{ASR} dA = \int_{uf=0}^{uf=uf_{total}} \frac{I_{max}}{-\frac{1}{2 \cdot F} \left[ \Delta^r G_{H_2(T)} + T \cdot R \cdot \ln \left( \frac{P_{H_2O(uf)}}{P_{H_2(uf)} \cdot \sqrt{P_{O_2(uf)}} \cdot \sqrt{P_0}} \right) \right] - V_{Cell}} duf \quad (19)$$

The power density is determined by the numerical solution of Eq. (19) in combination with Eq.

A fixed cell area of  $1 \text{ cm}^2$ , a temperature of  $800^\circ\text{C}$ , a total pressure of 1 bar, an oxygen partial pressure of 0.21 bar and an area specific resistance of  $1 \text{ }\Omega\text{cm}^2$  are chosen to compare the cell performances at uniform conditions. The total current  $I_{total} = 0.3\text{A}$  and the molar hydrogen fraction at the outlet of the anode  $x_{H_2} = 0.299$  are kept constant as well. Hence, the hydrogen flow rate and the hydrogen fraction at the entry of the anode are adjusted to obtain the linear and non-linear dependency of Nernst voltage from the fuel utilization. The calculation results of each case are summarized in Table 1.