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Modelling of anode delamination in solid oxide electrolysis cell and analysis of its effects on electrochemical performance



HYDROGEN

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ABSTRACT

Degradation of a solid oxide electrolysis cell (SOEC) during long-term operation remains to be the key obstacle to their massive production and commercialization. One of degradation processes within SOEC is anode delamination. The anode of SOEC splits at the interface with solid electrolyte due to elevated pressure of oxygen that is produced by electrochemical reactions. The main assumption that anode delamination starts at the fuel inlet is based on post-mortem analysis of SOEC. This paper addresses numerical modelling of a single, electrolyte supported, SOEC. The anode delamination is modelled by implementing the modifications of SOEC's geometry. A brief overview of the model is also given. Verification of the implemented model relies on the measurement data from literature. The simulation results show that increasing the area of delaminated anode (A_{delaminated}) increases the operating voltage of the SOEC if a constant electrolysis current is applied. This strongly influences the conversion efficiency (η) of the SOEC. Indeed, if linear growth of A_{delaminated} over time is assumed, the η of SOEC degrades very fast at the beginning of SOEC's operation. The presented model also helps analyze the hot spots of current density, where high pressure of oxygen appears.

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Introduction

The global energy consumption has been increasing very fast in the last few decades. Consequently, the pollution caused by burning fossil fuels increases [1]. Hence the utilization of renewable energy sources has emerged as a viable option to reduce pollution rates. The renewable energy sources (e.g. solar or wind energy) are site-specific and intermittent by their nature, so it seems reasonable to use excessive renewable energy for producing a fuel that can be stored and, when the energy is unavailable, efficiently re-used [2]. The electrolysis of water (H₂O), which is an abundant element on our planet, is a promising way to produce hydrogen (H₂). The H₂ is a clean, storable and transportable energy carrier [3-5]. It can be directly converted into electricity by fuel cells without producing greenhouse gases (e.g. carbon dioxide).

The solid oxide electrolysis cell (SOEC) technology is becoming increasingly interesting now, since it provides carbon-free production of H_2 [6]. SOEC can be used also in coelectrolysis process for production of syngas, which consist of H_2 and carbon monoxide (CO), where H_2O and carbon dioxide (CO₂) are consumed [7]. The consumption of CO₂ may be important to reduce the fraction of greenhouse gases in the atmosphere and mitigate the global warming.

Besides the benefit for environment, SOECs have some other advantages. SOECs can achieve higher conversion efficiency (η) of electrical to chemical energy compared to

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common electrolysis devices, since they operate at high temperature (T > 650 °C), in contrast to common devices that operate at low T [8]. High T allows that a part of the electrical energy, which is needed for electrolysis, is replaced by thermal energy. An example is waste heat in nuclear reactors that operate at high T. Therefore, high-temperature operation could be advantageous in a sense that SOEC efficiently utilizes waste heat for production of hydrogen [9].

The η of the SOEC should be calculated with care and thermodynamic limitations must be considered properly. For more details, the interested reader is referred to a sound study about η of the electrolysis and fuel cells [10]. An advantage of operation at high T is lower electrolyte's ohmic resistance and higher electrode's reaction kinetics [11]. The latter allows that a noble metal, such as platinum (Pt), which is commonly used for electrodes at low-temperature electrolysis, is replaced by less precious oxide ceramic material, such as nickel (Ni) doped yttria-stabilized zirconia (YSZ) or lanthanum strontium manganite (LSM), so the production costs are greatly reduced [8].

Despite many efforts to improve life-time of the SOECs, and make them economically viable, it seems that relatively fast degradation processes within these devices are still the major obstacles to massive production and commercialization. The degradation occurs due to different reasons so that three main types of degradation are distinguished: chemical/ electrochemical degradation, structural degradation and mechanical failure caused by thermal stress, as explained in Ref. [12]. One of the most critical structural degradation processes that occurs during long-term operation is delamination of the oxygen (O2) electrode at the interface with electrolyte. This process has been extensively investigated by a number of researchers [13–18]. This phenomenon has been studied from various perspectives. To gain more profound understanding of delamination a detailed first principles electrochemical model for degradation of SOECs is proposed in Ref. [13]. The model relies on local equilibrium in oxygen ion conductors that are in global thermodynamic non-equilibrium.

On the other hand, experimental studies have been undertaken to get evidences on degradation of O_2 electrodes in SOEC. In Ref. [14] different techniques (i.e. X-ray fluorescence, four-point resistivity, scanning electron microscopy - SEM, energy dispersive spectroscopy - EDS, X-ray diffraction and Raman micro-spectroscopy) for analysis of microstructural properties after a long-term operation have been applied.

It was found that high production rate of O_2 at the interface between anode and electrolyte causes a greater ability of zirconia to release O_2 and a lesser ability of the anode material to transfer O_2 ions through the anode layer. As a result, more O_2 would be produced than released into the air flow channel, so the pressure would increase and cause a crack that could initiate anode delamination.

Anode supported, YSZ-based, micro-tubular, solid oxide fuel cells (SOFCs) were tested at high voltages (up to 2.8 V, under electrolysis mode) in Ref. [15]. It was found that high partial pressure of O_2 at the interface between the O_2 electrode and electrolyte caused degradation of adjacent regions. This effect causes delamination of the O_2 electrode and such degradation also increases the impedance of the tested SOFCs.

The first-principles, density-functional-theory (DFT) calculations and thermodynamic modelling were employed to reveal the main processes that cause delamination in typical SOEC device made of YSZ electrolyte and Sr-doped LaMnO3 (LSM) O₂ electrode [16]. Another study showed a durability test of anode-supported SOFC that was operated for 9000 h as SOEC with a current density (J) of 1 A cm^{-2} [17]. The long-term tests show a voltage increase of about 40 mV kh⁻¹, which results in overall voltage degradation rate of 3.8% kh⁻¹. Similar voltage degradation rates were observed in Ref. [18]. The tested device operated at T = 800 °C and alternating $J = \pm 300 \text{ mA cm}^{-2}$ (repeated SOFC or SOEC operation cycle). At constant galvanostatic conditions (constant J) the cell had higher voltage degradation (5.9%) under electrolysis mode than under fuel cell mode (2.7%). There are a lot of studies that show area specific resistance (ASR) [19], current-voltage (J-V) characteristic [20] or impedance (Z) [21] of SOECs after a longterm operation under specific test conditions. Although these studies are valuable, good understanding of complex processes is needed. For that purpose, it is reasonable to build a model that is capable to predict the performance of degraded SOEC.

There are some papers that focus on SOEC or SOFC modelling [22–26], but no paper presenting a model of SOEC with delaminated anode has been found. Thus, to the best of the authors' knowledge, there is a gap in modelling of anode delamination on the device level.

This paper focuses on modelling of anode delamination and studies the effects of partly delaminated anode on electrochemical performances of modelled SOEC by means of numerical simulations. The aim is to understand how locally increased electrolyte J can elevate the pressure of O_2 as the O_2 is produced by the electrochemical reactions. The main novelty of this paper is modelling of degraded SOEC on device level and analysis of anode delamination effects on electrochemical performances of the SOEC.

Modelling

Two-dimensional (2-D), axisymmetric structure of SOEC was modelled in COMSOL Multiphysics[®] 4.3, as shown in Fig. 1. The data about the structure geometry, dimensions, materials, and most of input parameters were adopted from the literature [27]. Some of input parameters for this SOEC model were estimated from other experimental data or fitted accordingly, as explained in Section Model fitting.

Table 1 shows dimensions of each layer in the modelled SOEC. It is considered that modelled SOEC structure operates within a sealed chamber where constant T = 800 °C is maintained. The flow rate of hydrogen (H₂) fuel gas, containing 40%, 60%, or 80% of water (H₂O) steam, is 150 cm³ min⁻¹, whereas an open air is used at air electrode, as explained in Ref. [27]. The electrochemical performances of the real electrolysis cell were initially tested at J = -0.8 A cm⁻². The next step was measuring the *J*-V curves when the cell operated as SOEC (negative *J*) or as SOFC (positive *J*). In order to simulate the *J*-V curves of the modelled SOEC, a set of governing equations has to be implemented for each subdomain of this SOEC model, and solved with appropriate numerical method (e.g.



Fig. 1 - Two-dimensional (2-D), axisymmetric structure of a single, electrolyte supported, SOEC.

Table 1 - Dimensions of the modelled SOEC [27].			
Property	Symbol	Value	
Thickness of LSCF anode (air electrode)	da	25 µm	
Thickness of YSZ electrolyte (under electrode)	d _{e,e}	40 µm	
Thickness of YSZ electrolyte (maximum)	$d_{e,total}$	410 µm	
Thickness of Ni-YSZ cathode (fuel electrode)	d _c	100 µm	
Radius of alumina tube	rout	9.4 mm	
Radius of the fuel channel (inside the tube)	r _{in}	6.0 mm	
Radius of active SOEC	r _{cell}	2.25 mm	

iteratively with fully coupled solver that is included within COMSOL Multiphysics[®] 4.3) by parametric sweep. In the next subsections, a brief overview of equations with corresponding boundary conditions is given.

Gas channels

The fuel gas channel (below the SOEC's cathode) is formed inside the alumina tube, whereas the air channel (above the SOEC's anode) is open to surrounding air, as can be seen in Fig. 1. The flow of gases is modelled according to Eqs. (3)-(17)in Ref. [28]. The viscosities, thermal conductivities and specific heats at constant pressure are taken from Table 3, whereas molar masses and diffusion volumes of gas species are taken from Table 4 in Ref. [29].

The boundary conditions are specified as following. The inlet flux of fuel gases ($H_2 + H_2O$) is directed along the z-axis. The velocities (v_i) and mass fractions (Y_i) of gas species over the entire cross-section area of the fuel (cathode) inlet are homogeneous. The inlet velocity of fuel gas is denoted with $v_{in,fuel}$. It should be noted that $v_{in,fuel}$ is calculated by

Table 2 — Physical properties of porous electrodes in modelled SOEC.

Physical property	Symbol	Value	Unit	Ref.
Porosity of LSCF anode	ε _{p,a}	0.30	/	[25]
Porosity of Ni-YSZ cathode	ε _{p,c}	0.26	/	[25]
Effective electronic conductivity of porous anode	$\sigma_{\rm sa,eff}$	30000	$\mathrm{S}~\mathrm{m}^{-1}$	[25]
Effective electronic conductivity of porous cathode	$\sigma_{\rm sc,eff}$	1000	$\mathrm{S}~\mathrm{m}^{-1}$	[25]
Effective thermal conductivity of porous anode	$k_{\rm sa,eff}$	3.0	$\mathrm{W}~\mathrm{m}^{-1}~\mathrm{K}^{-1}$	[28]
Effective thermal conductivity of porous cathode	$k_{\rm sc,eff}$	3.0	$\mathrm{W}~\mathrm{m}^{-1}~\mathrm{K}^{-1}$	[28]
Anode material specific heat	$C_{p,a}$	573	$\mathrm{J~kg^{-1}~K^{-1}}$	[28]
Cathode material specific heat	$C_{p,c}$	595	$\mathrm{J~kg^{-1}~K^{-1}}$	[28]
Anode material specific density	$ ho_{a}$	6570	${ m kg}~{ m m}^{-3}$	[28]
Cathode material specific	$ ho_{c}$	6870	${\rm kg}~{\rm m}^{-3}$	[28]
density				

Table 3 – Physical properties of porous catalyst layers in modelled SOEC [25].

Physical property	Symbol	Value	Unit
Anodic exchange current density	i _{0,a}	$2.47 \cdot 10^{3}$	$\mathrm{A}~\mathrm{m}^{-2}$
Cathodic exchange current density	i _{0,c}	$1.56 \cdot 10^{4}$	$\mathrm{A}~\mathrm{m}^{-2}$
Anodic charge transfer	α_a^a	0.5	/
coefficient, anode			
Cathodic charge transfer	α_{c}^{a}	$1 - \alpha_a^a$	/
coefficient, anode			
Anodic charge transfer	α_a^c	0.4	/
coefficient, cathode			
Cathodic charge transfer	α_{c}^{c}	$1 - \alpha_a^c$	/
coefficient, cathode			

Table 4 $-$ Limiting, initial and final values of parameters.			
Parameter/Value	Limiting	Initial	Final
	$(\Delta x_{j,\max})$	$(x_{j,initial})$	(x _{j,final})
i _{0,a}	50 A m^{-2}	2470 A m^{-2}	2010 A m^{-2}
i _{0,c}	$100 \text{ A} \text{ m}^{-2}$	15600 A m^{-2}	$13870 \mathrm{~A~m^{-2}}$
αaa	$2.5 \cdot 10^{-3}$	0.250	0.275
αac	$2.5 \cdot 10^{-3}$	0.250	0.205
αa	/	0.750	0.725
α _c	/	0.750	0.795

considering flow rate of fuel (150 cm³ min⁻¹) and assuming the inlet flux with $r_{in,fuel} = 2.0$ mm in the middle of the tube. The $v_{in,fuel}$ equals 0.2 m s⁻¹ and it is used as boundary condition. The outlet velocity is determined by defining a constant pressure $p_{ref} = 1.013$ bar of the gas mixture at the outlet. The velocity (v_i) of gas fluxes at the surfaces within the gas channel is determined by no-slip boundary condition that assumes $v_i = 0$ m s⁻¹. The inlet mass fractions of gas species in the fuel are: $Y_{in,H2} = 0.143, 0.069, 0.027, and Y_{in,H2O} = 0.857, 0.931, 0.973, respectively. The inlet mass fractions of gas species in the air are: <math>Y_{in,O2} = 0.230$, $Y_{in,N2} = 0.770$. These are used as boundary conditions by considering the pressure ($p_{amb} = 1.013$ bar) of surrounding air. The modelled axisymmetry also demands that no flux passes the r-z plane, as seen in Fig. 1.

Porous electrodes

The continuity, momentum and species conservation equations are implemented to model the flow of gases within the porous electrodes [29]. For details, please refer to Eq. A1–4 in Appendix. In this model, the steam reforming of methane and water-gas-shift (WGS) reactions are omitted since the experimental test was performed by feeding the SOEC/SOFC with fuel gas mixture that consisted of H₂ and H₂O only [27], so the sources S_i should be zero within porous electrodes. Charge and energy conservation equations are basically the same as presented in Ref. [29], please refer to Eq. A5 and A6 in Appendix. The values of physical parameters are shown in Table 2.

Catalyst layers

The implemented equations for modelling the flow of gas species, charge and heat transfer in catalyst layers are basically the same as those presented in previous sections. At the interface between the porous cathode and catalyst layer, the hydrogen (H₂) is produced and the water (H₂O) is consumed, whereas at the interface between the porous anode and catalyst layer, the oxygen (O₂) is produced when the cell operates in SOEC mode. The anodic/cathodic current density $i_{a/c}$ is defined by Butler-Volmer equation:

$$\begin{split} \dot{i}_{a/c} = & i_{0,a/c} \cdot \left[C_{R,a/c} \cdot exp \left(\frac{\alpha_a^{a/c} \cdot F \cdot \eta_{act,a/c}}{R \cdot T} \right) - \right. \\ & C_{O,a/c} \cdot exp \left(- \frac{\alpha_c^{a/c} \cdot F \cdot \eta_{act,a/c}}{R \cdot T} \right) \right]. \end{split}$$
(1)

The $i_{0,a/c}$, $\alpha_{a/c}$ and $\eta_{act,a/c}$ are anodic/cathodic exchange current density, charge transfer coefficient and activation overpotential, respectively, F = 96485 As mol⁻¹ is Faraday

constant, R = 8.314 J mol⁻¹ K⁻¹ is the ideal gas constant and T is operating temperature of the SOEC. Concentration dependent coefficients (C_R for reduced species and C_O for oxidized species) are added into the Butler-Volmer equation to obtain J-V characteristics that fit the measured J-V characteristics reasonably well:

$$C_{R,a} = \begin{cases} 1; & J < 0(\text{SOEC}) \\ \frac{p_{O_2}}{p_{O_2,\text{ref}}}; & J > 0(\text{SOFC}) \end{cases}, C_{O,a} = \begin{cases} \frac{p_{O_2}}{p_{O_2,\text{ref}}}; & J < 0(\text{SOEC}) \\ 1; & J > 0(\text{SOFC}) \end{cases},$$
(2)

$$C_{R,c} = \begin{cases} \frac{p_{H_2O}}{p_{ref}}; & J < 0(SOEC) \\ \frac{p_{H_2,ref}}{p_{ref}}; & J > 0(SOFC) \end{cases}, C_{O,c} = \begin{cases} \frac{p_{H_2O,ref}}{p_{ref}}; & J < 0(SOEC) \\ \frac{p_{H_2}}{p_{ref}}; & J > 0(SOFC) \end{cases}.$$
(3)

Table 3 displays the parameters used as inputs for modelling the J in anode/cathode catalyst layers, including their values, units and references. Please note the thickness of anode/cathode catalyst layer is 25 μ m and constant values of the $i_{0,a/c}$ are defined. However, the presented values are used in baseline model. The model is further refined by optimization of specified parameters, as described in Section Model fitting.

The open circuit voltage (V_{oc}) of the SOEC is calculated by using Nernst equation:

$$V_{oc} = V^{0} + \frac{R \cdot T}{4 \cdot F} \cdot \ln\left(\frac{\left(\frac{p_{H_{2}}}{p_{ref}}\right)^{2} \cdot \left(\frac{p_{O_{2}}}{p_{amb}}\right)}{\left(\frac{p_{H_{2}O}}{p_{ref}}\right)^{2}}\right).$$
(4)

The V⁰ denotes standard cell potential at T = 800 °C and it equals 0.978 V in this case. The V_{oc} depends on partial pressures of hydrogen (p_{H2}), oxygen (p_{O2}) and water (p_{H2O}), which are determined according to the inlet mass fraction Y_{in,H2}, Y_{in,O2} and Y_{in,H2O}, respectively.

The energy transport is modelled according to Eq. A6, whereas the heat sources and sinks are modelled according to Eq. A7–13 in Appendix. It should be noted that a constant standard enthalpy change of formation of hydrogen $\Delta H_{H_2} = -241$ kJmol⁻¹ [30] is considered in Eq. A7 since no reliable data regarding its temperature dependence was found.

Electrolyte

The charge and heat transfer through dense (non-porous) electrolyte is modelled by similar equations as Eq. A5 and A6. Details can be found in Ref. [29]. The specific thermal conductivity $k_{\rm el}$ equals 2 W m⁻¹ K⁻¹ [28]. The $\sigma_{\rm el}$ is specific ionic conductivity of electrolyte. Its value varies with T with respect to mole fraction of Y₂O₃ in YSZ, annealing temperature and annealing time [31]. As seen from conductivity plot of sample I in Fig. 4 [31], $\sigma_{\rm el}$ is about 2 S m⁻¹ at 800 °C. The $\sigma_{\rm el}$ can also be calculated from the following equation [28]:

$$\sigma_{\rm el} = 3.34 \cdot 10^4 \cdot \exp\left(-\frac{10350 \rm K}{\rm T}\right) [\rm S \ m^{-1}], \tag{5}$$

where T is operating temperature of SOEC (or SOFC). Roughly the same value of $\sigma_{\rm el}$ (i.e. 2.16 S m⁻¹) is obtained if T = 1073 K (800 °C) is considered. Thus, $\sigma_{\rm el} = 2.1$ S m⁻¹ is used as input



Fig. 2 – Calculated J-V curves from initial (dashed lines)/ final (solid lines) values of parameters and measured J-V curves (symbols) from Fig. 2 in Ref. [27].

parameter of the presented SOEC model since no measurement data about σ_{el} can be found in Ref. [27].

Contacts

The metallic contacts (Pt mesh) allow the connection of SOEC with electric power source. Ideal contacts (i.e. contacts without electrical resistance) are assumed here for simplicity. The continuity of *J* is applied at the interfaces between the contacts and porous electrodes. Dirichlet boundary condition with constant electrostatic potential (ϕ_s) is applied on the top (+anode, $\phi_s = V_{cell}$) and bottom (–cathode, $\phi_s = 0$) contact of the SOEC.

It should be noted that boundary condition on the top contact can be modified in a manner that a constant inward current density (j_0) is applied instead of constant V_{cell} . This is especially convenient when *J*-V characteristics are calculated by varying the j_0 , i.e. by parametric sweep of the j_0 .

Model fitting

The implemented model that is intended for numerical investigations on how a variation of certain physical property reflects on electrochemical performances of the SOEC should be verified by experimental results. This is usually cumbersome task since some input parameters of the model are unknown or cannot be measured, so it demands a lot of knowledge about the physical background, experience and time to fit model as close as possible to a real device. The input parameters that directly affect the electrochemical performances of modelled SOEC are $i_{0,a/c}$ and $\alpha_{a/c}^{a/c}$. These are commonly termed empirical constants to fit the numerical results with experimental data [32]. The optimization of these parameters might be the simplest way to obtain close match between the calculated and measured *J*-V characteristics. However, it may be misinterpreted that *J*-V characteristics are



Fig. 3 – 2-D plot of a) normal electrolyte current density (J_{el}) in A m⁻², b) temperature (T) in Kelvin (K), and c) oxygen mole fraction (X_{O2}) within modelled SOEC. The SOEC operates at electrolysis current density (J) of –1 A cm⁻² and ambient temperature $T_{amb} = 800$ °C. A schematic of the modelled SOEC structure is added to make interpretation of 2-D plots easier.



Fig. 4 – The 2-D geometry of the axisymmetric, electrolyte supported, SOEC with partly delaminated anode. The delaminated surface is modelled by the area ($A_{delaminated}$) of the circle with radius $r_{delaminated}$.

simple polynomial curves, since these are actually exponential curves. It was shown that fitting SOEC and SOFC part of *J*-V characteristic should be done separately and requires more attention [32]. This is why $i_{0,a/c}$ and $\alpha_{a/c}^{a/c}$ are chosen for optimization.

Optimization algorithm

In literature, a plenty of optimization algorithms can be found, from simplex method for function minimization [33], to more complicated algorithms for real-time optimization [34]. In this case, a modified Newton-Raphson scheme was implemented in MATLAB[®] R2016b to find optimum values of vector x iteratively. The vector x consists of four elements: $x_1 \equiv i_{0,a}, x_2 \equiv i_{0,c}, x_3 \equiv \alpha_a^a$ and $x_4 \equiv \alpha_a^c$, which were optimized by the following algorithm:

$$\begin{split} x_{j}[k+1] &= \begin{cases} x_{j}[k] - \Delta x_{j}[k]; & |\Delta x_{j}[k]| < \Delta x_{j,max} \\ x_{j}[k] - \frac{2 \cdot \Delta x_{j,max} \cdot \Delta x_{j}[k]}{\Delta x_{j,max} + |\Delta x_{j}[k]|}; & |\Delta x_{j}[k]| \ge \Delta x_{j,max} \end{cases}, \text{where} \\ \Delta x_{j}[k] &= \frac{f(\overrightarrow{x}[k])}{\partial f(\overrightarrow{x}[k])/\partial x_{j}[k]} \end{split}$$
(6)

The cost function f is a sum of squared errors, i.e. differences between calculated and measured voltages from J-V curves:

$$f = \sum_{i=1}^{N} \left(V_{calc}[i] - V_{meas}[i] \right)^2$$
(7)

where $V_{calc}[i]$ represents calculated, whereas $V_{meas}[i]$ represents measured voltage, taken at the same *J* from *J*-V curves in Fig. 2 [27]. It should be noted that N = 41 values from *J*-V curves were considered in this optimization procedure. A partial derivative of function $(\partial f/\partial x_j)$ was calculated from three values

of f that were obtained at three equidistant values of x_i (i.e. minimum, central and maximum value of x_i) by considering square approximation around the central value. The parameter increment (Δx_i) was limited by setting the $\Delta x_{i,max}$ to prevent some problems when using the Newton-Raphson scheme (e.g. high increment may cause negative value of a specific parameter). Table 4 shows limiting, initial (i.e. set before optimization procedure) and final (i.e. obtained after optimization procedure) values of parameters. Limiting values were set manually by some experiments. Initial values should be roughly estimated to start optimization procedure. The initial $i_{0,a/c}$ were taken from Table 3, whereas the initial $\alpha_a^{a/c}$ were set to 0.250 to speed up the calculation. Please note that $\alpha_c^{a/c} = 1 - \alpha_a^{a/c}$ were calculated at each iteration of optimization, as already shown in Table 3. Optimization was performed by MATLAB® R2016b through "LiveLink" connection with COMSOL Multiphysics® 4.3. The final results were obtained after ten iterations when the f dropped below the specified value ($9 \cdot 10^{-3}$).

Comparison of calculated and measured J-V curves

After the optimization the final values of fitting parameters were used in the SOEC model. Fig. 2 shows calculated *J*-V curves from initial (dashed lines)/final (solid lines) values of parameters ($x_{j,initial}/x_{j,final}$) and measured *J*-V curves (symbols), which were copied from Fig. 2 in Ref. [27]. For model verification three different mixtures of hydrogen (H₂), containing 40%, 60%, and 80% of water (H₂O), were used.

As can be seen in Fig. 2, J-V curves strongly depend on mole fraction of H_2O in the fuel gas. The dashed J-V curves (calculated from initial values of parameters) strongly deviate from measured J-V curves if SOEC operation (J is negative) or SOFC operation (J is positive) is observed. The solid J-V curves (calculated from final values of parameters) match well with measured J-V curves in both modes of operation (i.e. SOEC or SOFC mode). Table 5 summarizes the statistical data about dashed and solid J-V curves. The mean squared error (MSE) is calculated according to:

$$MSE = \frac{1}{N} \sum_{i=1}^{N} (V_{calc}[i] - V_{meas}[i])^{2},$$
(8)

whereas the standard deviation (SD) is calculated as following:

$$SD = \sqrt{\frac{\sum\limits_{p=1}^{N} \left((V_{calc}[p] - V_{meas}[p]) - \sum\limits_{r=1}^{N} (V_{calc}[r] - V_{meas}[r]) / N \right)^{2}}{N - 1}}.$$
(9)

It should be mentioned that statistical data in Table 5 were calculated from N=41 samples (these can be noticed

Table 5 – Statistical data about J-V curves.			
J-V curve/Statistical data	MSE [V ²]	SD [mV]	
Dashed lines (from initial values of parameters, x _{i initial})	$1.34 \cdot 10^{-3}$	33	
Solid lines (from final values of parameters, x _{i final})	$0.22 \cdot 10^{-3}$	15	

as symbols in Fig. 2). It is obvious that using final (optimized) instead of initial parameters as inputs for implemented SOEC model gives much better match between the calculated and measured J-V curves. Finally, it has to be stressed that the measured values were manually read from plots in Fig. 2 [27], so the data are uncertain due to reading errors. However, it can be concluded that the optimized parameters resulted in a good match between the calculated and measured J-V curves, what is confirmed by low values of MSE and SD in Table 5.

Anode delamination modelling

One of the most critical degradation processes that occurs within SOEC during long-term operation is delamination of the O₂ electrode at the interface with electrolyte. The main obstacles in modelling seem to be very complex physical background of the anode delamination process and a lack of experimental data due to expensive and time consuming tests of SOEC degradation. Due to limited knowledge and unavailable experimental data about long-term degradation of SOEC's electrochemical performance in Ref. [27], a simple approach to model anode delamination was taken into consideration in this paper, as follows. The SOEC was simulated by considering the specified operating conditions in previous sections, i.e. $T_{amb} = 800$ °C, $p_{amb/ref} = 1.013$ bar, $Y_{in,H2} = 0.027$, $Y_{in,H2O} = 0.973$, J = -1 A cm⁻². Fig. 3 shows 2-D plot of a) normal electrolyte current density (Jel), b) temperature (T), and c) oxygen mole fraction (X_{O2}) within modelled SOEC. According to the simulation results in Fig. 3, it can be assumed that anode delamination starts in the middle of SOEC, since the highest Jel flows through the electrolyte in that point. This should potentially build up the local pressure of O₂, especially when a real SOEC would operate at high J, since electrochemical reactions that produce O₂ are proportional with J_{el} . Moreover, the highest T and X_{O2} also occur at that point. The former increases thermal stress at the interface between porous anode and electrolyte, whereas the latter confirms high production of O₂.

The highest J_{el} is observed in the center of O_2 electrode. Consequently, the highest amount of O_2 is released at that point. Post-mortem investigations of SOEC structures by SEM and other techniques showed the largest delaminated areas where the steam inlet was located [14]. These experimental results additionally confirm the aforementioned assumption since the steam inlet is also located in the center of the modelled SOEC. According to all these indications, the proposed SOEC model with modified geometry was built, as shown in Fig. 4.

The modified model includes a thin (about 10 μ m) insulation layer with radius $r_{delaminated}$, which serves to prevent the flow of J at the porous anode (LSCF)/electrolyte (YSZ) interface and thus mimics delaminated porous electrode (anode) of a real SOEC. This simple approach is based on experimental investigations of delaminated anode, as shown in SEM photographs that indicate splitting of the porous anode and electrolyte layers after a long-term operation of a real SOEC [14]. For modelling purposes, it is considered that Pt mesh (+/- contact) has infinite conductivity (i.e. assumed as

ideal conductor). This assumption allows setting Dirichlet boundary condition for electrostatic potential. Other governing equations with appropriate boundary conditions are the same as in Section Modelling.

Results and discussion

The analysis of static characteristics of the modelled SOEC is done in this section. First of all, J-V curves are calculated by considering different area of delaminated anode (A_{delaminated}). In order to show noticeable variations in J-V curves in Fig. 5a, the $r_{\text{delaminated}}$ is varied from 0.0 to 0.5 of the cell's radius (r_{cell}). This results in A_{delaminated}/A_{cell} ratio of 0.00, 0.01, 0.05, 0.10, 0.15, 0.20 and 0.25. Please note that A_{delaminated/cell} = $\pi \cdot r_{delaminated/cell}^2$. As can be seen in Fig. 5b, the voltage difference (ΔV) between the *J*-V curve of the SOEC with delaminated anode and the J-V curve of the SOEC with no anode delamination (A_{delaminated}/A_{cell} ratio is zero) is increased by approximately 0.15 V if the A_{delaminated}/A_{cell} ratio is increased to 0.25 and J = -1 A cm⁻² is applied to the anode. According to the simulation results, similar trends in J-V curves were observed if the inlet fuel contained a higher amount of hydrogen (i.e. 40% or 60% instead of 20% of H₂) and lower amount of water (i.e. 60% or 40% instead of 80% of H₂O). This is why those results are not shown in plots.

The electrical-to-fuel $\boldsymbol{\eta}$ of the modelled SOEC is calculated as follows:

$$\eta = \frac{\Delta G_{H_2} \cdot \iint_{A_{cathode}} i_c \cdot dA}{2 \cdot F \cdot J \cdot V \cdot A_{cell}},$$
(10)

where ΔG_{H2} is Gibbs free energy of formation, i_c is cathode current density, dA is differential area and A_{cell} is the area of active layers. Fig. 5c shows η of the SOEC with different $A_{delaminated}/A_{cell}$ ratio as a function of *J*. The η decreases with increasing the absolute value of *J*. Increasing the $A_{delaminated}/A_{cell}$ ratio also lowers the efficiency difference $\Delta \eta$, but the drop of $\Delta \eta$ is disproportional with increment of the $A_{delaminated}/A_{cell}$ ratio, as can been seen in Fig. 5d.

Fig. 6a shows area specific resistance (ASR) of modelled SOEC as a function of relative area of the delaminated anode ($A_{delaminated}/A_{cell}$ ratio). The ASR is calculated numerically from the slope of the *J*-V curve at a specific current density (J_0) by the following equation:

$$ASR|_{J_0} = \frac{\Delta V}{\Delta J}\Big|_{J_0} = \frac{V|_{J_0 - \Delta J_0} - V|_{J_0 + \Delta J_0}}{2 \cdot \Delta J_0},$$
(11)

where ΔV is voltage difference, ΔJ is current density difference, and ΔJ_0 is small increment of current density (equal to 1 mA cm⁻²). It can be noticed that ASR shows almost linear dependance of A_{delaminated}/A_{cell} ratio at J = -1 A cm⁻².

Actually, ASR shows small nonlinearity, as can be seen in Fig. 6a, and it also reflects on *J*-V curves, but its effect is hard to notice in Fig. 5a, whereas it is clearly seen in Fig. 5b. It can be noticed that ΔV also shows small nonlinearity and ΔV increases with $A_{delaminated}/A_{cell}$ ratio at J = -1 A cm⁻².

Fig. 6b shows efficiency (η) of modelled SOEC as a function of relative area of delaminated anode (A_{delaminated}/A_{cell} ratio). The η of the SOEC drops rapidly ($\Delta\eta$ drops by 0.12 at J = -1 A cm⁻², as seen in Fig. 5d) when the A_{delaminated}/A_{cell} ratio is increased



Fig. 5 – a) *J*-V curves, b) voltage difference, c) efficiencies and d) efficiency difference of modelled SOEC with partly delaminated anode. SOEC operates at ambient temperature $T_{amb} = 800$ °C and inlet hydrogen (H₂) fuel gas, containing 80% of water (H₂O).



Fig. 6 – a) Area specific resistance (ASR) and b) efficiency (η) of modelled SOEC as a function of relative area of the delaminated anode ($A_{delaminated}/A_{cell}$ ratio) at five different current densities: J = 0.001, 0.100, 0.250, 0.500 and 1.000 A cm⁻². SOEC operates at ambient temperature $T_{amb} = 800$ °C and inlet hydrogen (H₂) fuel gas, containing 80% of water (H₂O).

from 0 to 0.05. Furthermore, the η of the SOEC drops moderately ($\Delta\eta$ drops by 0.13 at $J=-1~A~cm^{-2}$, as seen in Fig. 5d) when the A_delaminated/A_cell ratio is increased from 0.05 to 0.25. From these observations it can be estimated that efficiency drops approximately four times faster when the A_delaminated/A_cell ratio is increased from 0 to 0.05. This suggests that efficiency of a real SOEC degrades very fast at the beginning of SOEC's operation. This holds true provided the A_delaminated/A_cell ratio progresses linearly with time. That assumption is justified by examining the polarization resistance R_p in Fig. 6 [27] that can be approximated by linear function of time t when t varies from 10 h to 50 h. Moreover, similar increment of ASR of about 0.08 Ω cm² at A_delaminated/A_cell = 0.15, $J = 0.001~A~cm^{-2}$ in Fig. 6a, can be noticed as that of R_p in Fig. 6 [27] if t varies from 10 h to 50 h. From the presented results it is obvious that the steady-state

simulation results cannot be directly linked with degradation processes of a real SOEC. A far more complex time-dependent SOEC model would be necessary to describe the anode degradation processes, considering e.g. high pressure of O₂. Details can be found in Ref. [13], where it is shown that electronic conduction through the electrolyte must be taken into account for determining local O₂ chemical potential (μ_{O2}) of the electrolyte. Under certain conditions, high pressures of O₂ can occur in the electrolyte just nearby the O₂ electrode/electrolyte interface, leading to O₂ electrode delamination. In this model, the electronic conduction in electrolyte is not considered due to simplification.

There is one obstacle in modelling anode delamination with COMSOL Multiphysics[®] 4.3, since the modifications of SOEC geometry are impossible (at least to the best of the



Fig. 7 – The normal electrolyte current density (J_{el}) in A m⁻² within the modelled SOEC that operates at ambient temperature $T_{amb} = 800$ °C and inlet hydrogen (H₂) fuel gas, containing 80% of water (H₂O). The area of the delaminated anode is 1% of the total cell area.

authors' knowledge) when parametric sweep or transient analysis is performed, so the modelling is restricted. The problem might be solved by introducing a thin resistive layer at the interface between porous anode and electrolyte, which would also increase the ASR, but it would not perturb the spatial distribution of $J_{\rm el}$ equally as the partly delaminated anode does.

To illustrate the importance of anode delamination modelling, the $J_{\rm el}$ within the SOEC ($A_{\rm delaminated}/A_{\rm cell} = 0.01$) is shown in Fig. 7. As can be seen, the anode active layer (electrode) is delaminated from its center (at r = 0 mm) to $r_{\rm delaminated} = 0.225$ mm. The *J* cannot flow through the electrode in vertical direction (z-axis), since the crack below the electrode does not conduct electric current. Due to this, *J* flows in radial direction (r-axis) and it is concentrated at the junction with electrolyte layer. As a consequence, $J_{\rm el}$ is locally increased by about two times ($J_{\rm el,max} = 1.8 \cdot 10^4$ A m⁻² if average current density $J_{\rm avg} = 10^4$ A m⁻² is applied on the electrode).

Local current densities (i.e. electronic and ionic) within the real anode active layer could be even higher than presented due to its porous structure and non-ideal contact with electrode and electrolyte layer. This might have serious impact on increasing the pressure of O_2 after a certain time the anode delamination had been initiated. However, a refined anode delamination model should be used to obtain deep insight into local degradation processes.

The main contribution of presented paper is analysis of the electrochemical performances of SOEC and critical spots at the interface between porous anode and electrolyte that cause pressure build-up, and consequently, progressing anode delamination. The proposed model has its potential to be further developed by coupling the local pressure build-up and mechanical properties (e.g. ultimate tensile strength) at the interface between porous anode and electrolyte to investigate the evolution of anode delamination over a period of time.

Conclusions

Two-dimensional (2-D), axisymmetric, SOEC was modelled in COMSOL Multiphysics[®] 4.3. The modelled structure comprises gas channels, porous anode and cathode active layers, solid electrolyte and contacts. A brief overview of implemented model that consists of continuity, momentum, species, charge and energy conservation equations with appropriate boundary conditions was presented.

Since some input parameters, which are essential to calculate static characteristics of the modelled SOEC, were unknown, the optimization algorithm was elaborated to tune anodic/cathodic exchange current density ($i_{0,a/c}$) and anodic/cathodic charge transfer coefficient for anode/cathode ($\alpha_{a/c}^{a/c}$). The optimized parameters were used in the model to obtain a good fit between calculated and measured current-voltage (*J*-V) curves, which was confirmed by low standard deviation (SD = 15 mV) of N = 41 samples of V from *J*-V curves, so the presented model was verified by measurement data from literature.

Next, the anode delamination modelling was proposed by considering the modifications of SOEC's geometry. A thin insulation layer was inserted between porous anode and electrolyte to model delaminated anode area with radius r_{delaminated}. It was assumed that delamination starts in the middle of the SOEC where the fuel (i.e. mixture of hydrogen and water) inlet is formed, as indicated by experimental studies.

The simulation results showed that increasing the relative area of delaminated anode (i.e. $A_{delaminated}/A_{cell}$ ratio) almost proportionally increases the operating voltage (V) of the SOEC, since the area specific resistance (ASR) promotes almost linearly with $A_{delaminated}/A_{cell}$ ratio. The increased $A_{delaminated}/A_{cell}$ ratio strongly influences the η of the SOEC. It was shown that η drops by approximately the same value when the $A_{delaminated}/A_{cell}$ ratio is increased from 0 to 0.05 as the $A_{delaminated}/A_{cell}$ ratio is increased from 0.05 to 0.25.

This result suggests that η degrades very fast at the beginning of SOEC's operational cycle if we assume that $A_{delaminated}/A_{cell}$ ratio promotes linearly with time.

The analysis of the J_{el} within the SOEC showed that J_{el} could be locally increased. The increased J_{el} might increase the local pressure of oxygen after a certain time the anode delamination had been initiated. According to the promising results in this study, the presented anode delamination model should be upgraded to obtain more detailed insight into local degradation processes. The upgrade should couple the local pressure build-up and mechanical properties at the interface between porous anode and electrolyte.

However, there are still many issues regarding the presented model that need to be addressed in the future. One of them is obviously how to relate delamination rate with respect to time. The major limitation seems to be a lack of knowledge about complex degradation processes, but also a challenging task to implement an appropriate model on device level.

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Appendix

• Continuity equation:

$$\vec{\nabla} \cdot \left(\rho \cdot \vec{v} \right) = S_m,$$
 A1

where ρ is the average density of gas, v is the velocity vector and S_m is the source (or sink) for the production (or consumption) of gas species that can be attributed to electrochemical reactions within the porous electrodes.

• Momentum equation:

The flow of gases in porous media is modelled by the following momentum equation:

 $D_{i,j,eff} = \epsilon_p^{3/2} \cdot D_{i,j}$, where $D_{i,j}$ is binary diffusion coefficient of gas species i and j:

$$\vec{j_i} = -\sum_{j=1}^{N-1} \rho \cdot D_{i,j,eff} \cdot \vec{\nabla} \ Y_j = -\sum_{j=1}^{N-1} \rho \cdot \epsilon_p^{\frac{3}{2}} \cdot D_{i,j} \cdot \vec{\nabla} \ Y_j. \tag{A4}$$

• Charge conservation equation:

$$\vec{\nabla} \cdot \left(-\sigma_{s/el,eff} \cdot \vec{\nabla} \phi_{s/el} \right) = S_{s/el,i},$$
 A5

The electronic/ionic current transport in porous electrodes is modelled by considering conservation of electric charge, where $\sigma_{s/el,eff}$ is effective electronic/ionic conductivity of porous electrode and $\phi_{s/el}$ is electrostatic potential in the solid/ electrolyte phase. It is assumed that no electrical current source ($S_{s,i} = 0$) is present within the solid (metal) phase.

• Energy conservation equation:

$$\vec{\nabla} \cdot \left(\left(\rho \cdot C_p \right)_{eff} \cdot \vec{\upsilon} \cdot T \right) = \vec{\nabla} \cdot \left(k_{s,eff} \cdot \vec{\nabla} \ T \right) + S_e. \tag{A6}$$

The energy transport in porous electrodes is modelled by using effective thermal conductivity ($k_{s,eff}$), and effective product of specific heat (C_p) and specific density (ρ) of the solid material. The heat source S_e depends on chemical (reversible), electrochemical (irreversible) and ohmic heat generation. The reversible heat term in SOEC cathode $q_{rev,c}$ is:

$$q_{\text{rev,c}} = \frac{i_c \cdot \Delta H_{H_2}}{2 \cdot F}, \qquad \qquad \text{A7}$$

where i_c is cathodic current density, $\Delta H_{H_2} = -241 \text{kJmol}^{-1}$ is the standard enthalpy change of formation, and F = 96485 As mol⁻¹ is Faraday constant. The irreversible heat term $q_{irr,c}$ is:

$$q_{\rm irr,c} = \dot{i}_{\rm c,eff} \cdot \eta_{\rm act,c}.$$
 A8

The ohmic heat term $q_{\text{ohm,c}}$:

where the $\sigma_{sc,eff}$ and $\sigma_{ec,eff}$ are effective cathode electronic and ionic conductivity. The total heat generation term $S_{e,c}$ is the sum of $q_{rev,c}$, $q_{irr,c}$ and $q_{ohm,c}$:

$$\frac{\rho}{\varepsilon_{p}}\left(\left(\vec{\overline{\upsilon}}\cdot\vec{\overline{\nabla}}\ \right)\frac{\vec{\overline{\upsilon}}}{\varepsilon_{p}}\right) = \vec{\overline{\nabla}}\cdot\left[-pI + \frac{\mu}{\varepsilon_{p}}\left(\left(\vec{\overline{\nabla}}\ \vec{\overline{\upsilon}}\right) + \left(\vec{\overline{\nabla}}\ \vec{\overline{\upsilon}}\right)^{T}\right) - \frac{2\mu}{3\varepsilon_{p}}\left(\vec{\overline{\nabla}}\ \vec{\overline{\upsilon}}\right)I\right] - \left(\frac{\mu}{\kappa} + \vec{\overline{\nabla}}\ \left(\rho\vec{\overline{\upsilon}}\right)\right)\vec{\overline{\upsilon}},$$
A2

where μ is viscosity of gases, ε_p is porosity and κ is permeability of the electrode media.

• Species conservation equation:

$$\vec{\nabla} \cdot \left(\rho \cdot \vec{\upsilon} \cdot \mathbf{Y}_{i} \right) = -\vec{\nabla} \cdot \vec{j}_{i} + \mathbf{S}_{i},$$
 A3

where j_i is the multicomponent diffusive mass flux vector, Y_i is mass fraction of a gas specie. Diffusion in porous media is commonly modelled by using effective diffusion coefficient

$$S_{e,c} = q_{rev,c} + q_{irr,c} + q_{ohm,c}.$$
 A10

The irreversible heat term $q_{irr,a}$ in the anode is calculated similarly:

$$q_{\rm irr,a} = \dot{i}_{\rm a,eff} \cdot \eta_{\rm act,a}.$$
 A11

The ohmic heat term $q_{ohm,a}$ is calculated as:

$$q_{\rm ohm,a} = \sigma_{\rm sa,eff} \cdot \vec{\nabla} \ \phi_{\rm s} \cdot \vec{\nabla} \ \phi_{\rm s} + \sigma_{\rm ea,eff} \cdot \vec{\nabla} \ \phi_{\rm el} \cdot \vec{\nabla} \ \phi_{\rm el}, \qquad A12$$

where the $\sigma_{sa,eff}$ and $\sigma_{ea,eff}$ are effective anode electronic and ionic conductivity. The total heat generation term $S_{e,a}$ is the sum of $q_{irr,a}$ and $q_{ohm,a}$:

$$S_{e,a} = q_{irr,a} + q_{ohm,a}.$$
 A13

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