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Modelling the dynamic response of a solid oxide steam electrolyser to transient inputs during renewable hydrogen production

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Abstract Hydrogen is regarded as a leading candidate for alternative future fuels. Solid oxide electrolyser cells (SOEC) may provide a cost-effective and green route to hydrogen production especially when coupled to a source of renewable electrical energy. Developing an understanding of the response of the SOEC stack to transient events that may occur during its operation with intermittent electricity input is essential before the realisation of this technology. In this paper, a one-dimensional (1D) dynamic model of a planar SOEC stack has been employed to study the dynamic behaviour of such an SOEC and the prospect for stack temperature control through variation of the air flow rate. Step changes in the average current density from 1.0 to 0.75, 0.5 and 0.2 A/cm² have been imposed on the stacks, replicating the situation in which changes in the supply of input electrical energy are experienced, or the sudden switch-off of the stack. Such simulations have been performed both for open-loop and closed-loop cases. The stack temperature and cell voltage are decreased by step changes in the average current density. Without temperature control via variation of the air flow rate, a sudden fall of the temperature and the cell potential occurs during all the step changes in average current density. The temperature excursions between the initial and final steady states are observed to be reduced by the manipulation of the air flow rate. Provided that the change in the average current density does not result in a transition from exothermic to endothermic operation of the SOEC, the use of the air flow

rate to maintain a constant steady-state temperature is found to be successful.

Keywords hydrogen production, renewable energy, solid oxide electrolyser cell, 1D dynamic model, dynamic behaviour, temperature control

1 Introduction

Hydrogen is regarded as a leading candidate for alternative future fuels. It has the potential to address the environmental and energy security issues associated with fossil-derived hydrocarbon fuels. Among many hydrogen production methods, water electrolysis is a well-established technique which, however, has not had a significant commercial penetration, mainly due to its high electricity consumption and related high operating cost [1, 2]. High temperature electrolysis is a promising alternative to the conventional lower temperature water electrolysis process. A combination of favourable thermodynamics and kinetics at high temperatures (500–1000°C) offers reduced electrical energy consumption per unit of hydrogen compared to low temperature water electrolysis, and thus may provide a cost-effective route to hydrogen production. This approach is particularly advantageous if a high temperature electrolyser may be simply and efficiently coupled to a source of renewable solar [3,4], geothermal [5,6], wind [4] or nuclear [7] electrical energies, to produce carbon-free hydrogen.

High temperature electrolysis is performed using a solid oxide electrolysis cell (SOEC), which can be seen in simple terms as the reverse operation of a solid oxide fuel cell (SOFC). An SOEC consists of a three-layer solid structure (composed of porous cathode, electrolyte and porous anode) and an interconnect plate. Steam is introduced at the cathode side of the solid structure where it is reduced into hydrogen, releasing oxide ions in

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the process. The oxide ions then migrate through the electrolyte to the anode where they combine to form oxygen molecules, releasing electrons. A number of repeating cells are normally packed into a stack to achieve a sufficient hydrogen production rate. During the operation of an SOEC system, heat is generated in the stack as a result of irreversible losses. An SOEC stack can function in either exothermic, endothermic or thermoneutral operating modes. In the exothermic operation mode, the temperature increases along the stack due to the heat accumulated from the irreversible losses. In the endothermic operation, the heat generated via irreversible losses is lower than the thermal energy consumed by the reaction, which results in a temperature decrease as the reaction proceeds along the stack. Finally, thermoneutral stack operation occurs when the thermal energy consumed by the reaction is precisely matched by the heat generated via irreversible losses. A change in operating conditions (such as stack temperature, average current density, operating voltage, steam utilisation and the inlet gas composition) can alter the operating mode of the stack.

As in SOFCs, the most common electrolyte material used in SOECs is yttria-stabilized zirconia (YSZ) which exhibits high oxygen ion conductivity and good mechanical strength. Typical materials for the cathode are nickel-YSZ cermets and those for the anode are perovskite oxides such as lanthanum strontium manganite (LSM). Ceramics like those used in SOECs are typically brittle materials exhibiting little plasticity and low fracture toughness, and subjected to stresses that can arise from manufacturing (residual stresses), differences between thermal expansion coefficients, temperature gradients along the cell, oxygen activity gradients, and/or external mechanical loading. In general, a mixture of all these sources of stress is likely to be present and their magnitude depends on the properties of the materials, operating conditions, and design. During the normal operation of a SOEC, the suppression of temperature gradients or transients that can cause excessive stresses within the SOEC components and lead to cell breakdown is crucial. Such problem becomes more severe when the operation of the SOEC is integrated with intermittent energy sources. Due to their intermittent nature, renewable energy resources—such as wind and solar energies—cannot produce power steadily, since their power production rates change with seasons, months, days, hours etc. Such variation in the electricity input may cause undesirable temperature fluctuations and significant thermal excursion within the SOEC stack. The operation of the SOEC should be guaranteed over an acceptable temperature range.

The development of an understanding of the response of the SOEC stack, especially its temperature profiles, to transient events that may occur during its operation with intermittent energy input is therefore essential before this technology can be deployed. The development of an

appropriate control strategy over temperature fluctuations is also desirable.

To capture the spatially-distributed stack performance (especially the temperature distribution during operation) and the transient behaviour of a stack when integrated with intermittent energy resources, a one-dimensional distributed dynamic model of a cathode-supported planar SOEC stack has been developed, with which some preliminary investigations on the operation of SOECs have been reported [8–10]. The model developed is employed here to predict the stack response during step changes in the average current density which might be caused by the time-dependent nature of the supply of electrical energy to the SOEC or the demand for hydrogen from the SOEC.

2 Description of the 1-D dynamic model

To ensure a sufficient rate of H_2 production, an SOEC system must consist of several repeating cells assembled in stacks. The models of such stacks are usually constructed for the smallest unit cell, which is assumed to describe the response of the whole stack subject to the use of adequate boundary conditions. Here, the modelled unit cell is considered to be in the centre of a sufficiently large stack that end effects are negligible. Although interconnects normally provide the gas flow channels above and below the solid structure, the effect of individual passages is neglected here. The pressure drop along the gas channels is also assumed negligible at the operating pressure of 0.1 MPa. For modelling purposes, the unit cell is considered to consist of four components, the cathode and the anode gas streams, the solid structure (which includes the two electrodes—cathode and anode, and electrolyte) and the interconnect. The schematic view of such a unit cell is shown in Fig. 1. The cathode stream inlet gas is composed of H_2 and H_2O . The addition of hydrogen in the cathode stream avoids the oxidation of materials that

Fig. 1 Schematic view of a unit cell of a planar SOEC stack

might be induced by using pure steam. Hydrogen can be circulated from that produced on the anode side. On the anode side, air is introduced to enable the temperature control of the stack; the air feed also permits the convective transport of the oxygen produced. The inlet air composition is assumed to be 21 mol% O₂/79 mol% N₂.

The model developed consists of an electrochemical model, mass balances for the gas streams, and energy balances for the cathode and anode streams, solid structure and interconnect.

2.1 Electrochemical model

An electrochemical model is used to relate variables such as gas species concentrations, cell component temperatures and average current density to the electrical potential of the cell, which can then be used to calculate the electrical energy consumption. The electrical potential is taken as constant along the cell as the electrodes are assumed to be good electronic conductors. As shown in Eq. (1), the cell potential corresponds to the sum of the reversible potential and all the irreversible losses that occur as the electrical current is passed through the cell. Such irreversible losses include Ohmic losses, cathode and anode concentration overpotentials, and cathode and anode activation overpotentials, which are all partly responsible for the heat produced within the cell. The calculation of these irreversible losses can be found in Refs. [8,10]. For the work reported in this paper, a contact resistance of 0.1 Ω·cm² between coating and interconnect has been taken into account for the irreversible losses in addition to those calculated in Refs. [8,10].

$$U = U^{\text{rev}}(x) + \eta_{\text{Ohm}}(x) + \eta_{\text{conc,cathode}}(x) + \eta_{\text{conc,anode}}(x) + \eta_{\text{act,cathode}}(x) + \eta_{\text{act,anode}}(x) + \eta_{\text{contact}} \quad (1)$$

The reversible potential is determined through the Nernst equation, which predicts the minimum electrical potential required to split H₂O at a particular location along the cell with a specific temperature and gas concentrations. Equation (2) has been derived assuming ideal gas behaviour. The solid structure temperature is applied in the Nernst equation as the reactions take place at the triple phase boundaries (TPBs) where the electrolyte, porous electrode and gas species meet at the interfaces between the electrolyte and the electrodes. U^0 represents the standard potential, which corresponds to the reversible potential calculated at unity activity. It is determined as a function of the Gibbs free energy change involved in the reaction, taking the partial pressures of H₂, H₂O and O₂ to be at standard pressure.

$$U^{\text{rev}}(x) = U^0(x) + \frac{\Re T_S(x)}{2F} \ln \left(\frac{C_{\text{H}_2}(x)(P_{\text{O}_2} \times 10^{-5})^{0.5}}{C_{\text{H}_2\text{O}}(x)} \right) \quad (2)$$

Ohmic losses are linearly proportional to the current density and can be determined through Ohm's law as shown in Eq. (3), where j and R_{Ohm} represent the local current density and local cell resistance, respectively. R_{Ohm} is calculated using the conductivity data of each layer of the solid structure. In Eq. (4), cross plane charge flow and series connection of resistances have been assumed. The conductivity of the electrodes is assumed constant along the cell while that of the electrolyte is estimated as a function of local temperature.

$$\eta_{\text{Ohm}}(x) = j(x)R_{\text{Ohm}}(x), \quad (3)$$

$$R_{\text{Ohm}}(x) = \frac{\tau_{\text{cathode}}}{\sigma_{\text{cathode}}} + \frac{\tau_{\text{electrolyte}}}{\sigma_{\text{electrolyte}}(x)} + \frac{\tau_{\text{anode}}}{\sigma_{\text{anode}}}. \quad (4)$$

Concentration gradients for the species develop in the porous electrode, if the fluxes of the reactant to, and the products away from, the TPBs are slower than that corresponding to the discharged electrical current. The cathode concentration overpotential is represented in Eq. (5). Equation (6) describes the anode concentration overpotential with air-fed anode channels. Note that the temperature of the gas mixture at the TPBs is represented by the solid structure temperature.

$$\eta_{\text{conc,cathode}}(x) = \frac{\Re T_S(x)}{2F} \ln \left(\frac{C_{\text{H}_2}^{\text{TPB}}(x)C_{\text{H}_2\text{O}}(x)}{C_{\text{H}_2}(x)C_{\text{H}_2\text{O}}^{\text{TPB}}(x)} \right), \quad (5)$$

$$\eta_{\text{conc,anode}}(x) = \frac{\Re T_S(x)}{4F} \ln \left(\frac{C_{\text{O}_2}^{\text{TPB}}(x)T_S(x)}{C_{\text{O}_2}(x)T_A(x)} \right). \quad (6)$$

The diffusion activities of H₂ and H₂O in the porous cathode are expressed in Eqs. (7) and (8), whilst the diffusion activity of O₂ in the porous anode is represented in Eq. (9), where $D_{\text{eff,cathode}}$ represents the average effective diffusivity coefficients in the cathode, considering a binary gas mixture of H₂ and H₂O; and $D_{\text{eff,anode}}$ represents the average effective diffusivity coefficient in the anode, considering a binary gas mixture of O₂ and N₂.

$$C_{\text{H}_2}^{\text{TPB}}(x) = C_{\text{H}_2}(x) + \frac{\tau_{\text{cathode}}}{2FD_{\text{eff,cathode}}} \cdot j(x), \quad (7)$$

$$C_{\text{H}_2\text{O}}^{\text{TPB}}(x) = C_{\text{H}_2\text{O}}(x) - \frac{\tau_{\text{cathode}}}{2FD_{\text{eff,cathode}}} \cdot j(x), \quad (8)$$

$$C_{O_2}^{TPB}(x) = C_{O_2}(x) + C_{N_2}(x) - C_{N_2}(x) \exp\left(\frac{-j(x)\tau_{anode}}{4FD_{eff,anode}[C_{O_2}(x) + C_{N_2}(x)]}\right). \quad (9)$$

Activation overpotentials are classically determined through the Butler-Volmer equation. The extended form of the Butler-Volmer equation is applied to account for the differences in the gas concentrations at the TPBs and in the bulk stream. Equations (10) and (11) are for the cathode

and anode activation overpotentials respectively. Although reactions are generally rapid and activation overpotentials tend to be small at high temperatures, they can become the most significant form of irreversible losses as the operating temperature is reduced.

$$j(x) = j_{0,cathode}(x) \left[\frac{C_{H_2}^{TPB}(x)}{C_{H_2}(x)} \exp\left(\frac{2(1-\alpha)F}{RT_S(x)} \eta_{act,cathode}(x)\right) - \frac{C_{H_2O}^{TPB}(x)}{C_{H_2O}(x)} \exp\left(\frac{-2\alpha F}{RT_S(x)} \eta_{act,cathode}(x)\right) \right], \quad (10)$$

$$j(x) = j_{0,anode}(x) \left[\exp\left(\frac{2(1-\alpha)F}{RT_S(x)} \eta_{act,anode}(x)\right) - \frac{C_{O_2}^{TPB}(x)}{C_{O_2}(x)} \exp\left(\frac{-2\alpha F}{RT_S(x)} \eta_{act,anode}(x)\right) \right], \quad (11)$$

where α (usually taken to be 0.5), $j_{0,cathode}$ and $j_{0,anode}$ represent the transfer coefficient and the exchange current density for the cathode and anode, respectively. Electrode exchange current densities are expressed in Eq. (12) as a function of the pre-exponential factor and activation energy. It is assumed that in an SOEC, the forward and backward reactions at each electrode as well as the electrode materials are the reverse of those in an SOFC. Hence the values used for k_{anode} and E_{anode} in previous ISOFC studies [11] have been substituted into k_{anode} and E_{anode} in the IT-SOEC model. The same assumption is used when assigning the values to the SOEC anode kinetic parameters. The parameters employed for the SOEC simulations are shown in Table 1.

$$j_{0,electrode}(x) = \frac{RT_S(x)}{2F} k_{electrode} \exp\left(\frac{-E_{electrode}}{RT_S(x)}\right), \quad (12)$$

electrode $\in \{\text{cathode}, \text{anode}\}$.

streams.

$$\begin{aligned} \frac{\partial}{\partial t}[C_i(x)] &= -u_C \frac{\partial}{\partial x}[C_i(x)] + \frac{1}{h_C} \nu_i R(x), i \\ &\in \{H_2, H_2O\}, \end{aligned} \quad (13)$$

$$C_i(0) = C_i^0, i \in \{H_2, H_2O\}, \quad (14)$$

$$R(x) = \frac{j(x)}{2F}, \quad (15)$$

$$\begin{aligned} \frac{\partial}{\partial t}[C_i(x)] &= -u_A \frac{\partial}{\partial x}[C_i(x)] + \frac{1}{h_A} \nu_i R(x), i \\ &\in \{O_2, N_2\}, \end{aligned} \quad (16)$$

$$C_i(0) = C_i^0, i \in \{O_2, N_2\}. \quad (17)$$

2.2 Mass balances

The composition of the cathode stream evolves along the cell as the H_2 / H_2O mixture moves towards the outlet. Such a composition change is tracked in the model using the cathode stream mass balance (as shown in Eqs. (13)–(15)) predicting the H_2 and H_2O concentrations at each location along the channel [8]. The anode stream mass balance (as shown in Eqs. (16) and (17)) predicts the O_2 and N_2 concentrations at each location along the stack [10]. The cathode and anode stream velocities are assumed constant (i.e. negligible frictional pressure drops along the stack) and determined from the outlet flow rate of the

2.3 Energy balances

In the energy balances, it is considered that the thermal fluxes between the gas streams and the solid parts of the cell are fully described by convection. The thermal fluxes along the solid parts of the cell are modelled using Fourier's law of heat conduction while radiative heat exchange is taken into account between the solid structure and the interconnect. The entire enthalpy change of the reaction is assumed to occur in the solid structure. Mean density and mean heat capacity values are applied in the anode and cathode energy balances. These are calculated as spatial averages of all the values along the cell. The

Table 1 Pre-exponential factor and activation energy for the exchange current density

$k_{cathode}/(\Omega^{-1} \cdot m^{-2})$	$k_{anode}/(\Omega^{-1} \cdot m^{-2})$	$E_{cathode}/(J \cdot mol^{-1})$	$E_{anode}/(J \cdot mol^{-1})$
6.54×10^{11}	2.35×10^{11}	1.40×10^5	1.37×10^5

remaining gas and material properties are taken to be constant along the cell. Equations (18)–(27) describe all the heat conduction mechanisms considered in this work.

$$\begin{aligned} \frac{\partial}{\partial t} [T_C(x)] = & -u_C \frac{\partial}{\partial x} [T_C(x)] \\ & + \frac{k_C}{\rho_C c_{p,C} h_C} [T_S(x) - T_C(x)] \\ & + \frac{k_C}{\rho_C c_{p,C} h_C} [T_I(x) - T_C(x)], \end{aligned} \quad (18)$$

$$T_C(0) = T_C^0, \quad (19)$$

$$\begin{aligned} \frac{\partial}{\partial t} [T_A(x)] = & -u_A \frac{\partial}{\partial x} [T_A(x)] \\ & + \frac{k_A}{\rho_A c_{p,A} h_A} [T_S(x) - T_A(x)] \\ & + \frac{k_A}{\rho_A c_{p,A} h_A} [T_I(x) - T_A(x)], \end{aligned} \quad (20)$$

$$T_A(0) = \frac{T_S(0) + T_I(0)}{2}, \quad (21)$$

$$\begin{aligned} \frac{\partial}{\partial t} [T_S(x)] = & \frac{\lambda_S}{\rho_S c_{p,S}} \frac{\partial^2}{\partial x^2} [T_S(x)] - \frac{k_C}{\rho_S c_{p,S} h_S} [T_S(x) - T_C(x)] \\ & - \frac{k_A}{\rho_S c_{p,S} h_S} [T_S(x) - T_A(x)] \\ & - \frac{2}{\rho_S c_{p,S} h_S} \left[\frac{\sigma [T_S(x)^4 - T_I(x)^4]}{1/\varepsilon_S + 1/\varepsilon_I - 1} \right] \\ & + \frac{1}{\rho_S c_{p,S} h_S} [-\Delta H(x)R(x) + j(x)U], \end{aligned} \quad (22)$$

$$\frac{\partial}{\partial x} [T_S(0)] = 0, \quad \frac{\partial}{\partial x} [T_S(L)] = 0, \quad (23)$$

$$\begin{aligned} \frac{\partial}{\partial t} [T_I(x)] = & \frac{\lambda_I}{\rho_I c_{p,I}} \frac{\partial^2}{\partial x^2} [T_I(x)] - \frac{k_C}{\rho_I c_{p,I} h_I} [T_I(x) - T_C(x)] \\ & - \frac{k_A}{\rho_I c_{p,I} h_I} [T_I(x) - T_A(x)] \\ & + \frac{2}{\rho_I c_{p,I} h_I} \left[\frac{\sigma [T_S(x)^4 - T_I(x)^4]}{1/\varepsilon_S + 1/\varepsilon_I - 1} \right], \end{aligned} \quad (24)$$

$$\frac{\partial}{\partial x} [T_I(0)] = 0, \quad \frac{\partial}{\partial x} [T_I(L)] = 0, \quad (25)$$

$$k_C = Nu_C \frac{\lambda_C}{d_{h,C}}, \quad k_A = Nu_A \frac{\lambda_A}{d_{h,A}}, \quad (26)$$

$$d_{h,C} = \frac{2Wh_C}{W + h_C}, \quad d_{h,A} = \frac{2Wh_A}{W + h_A}, \quad (27)$$

2.4 Temperature control

Temperature control is provided for an SOEC stack through the manipulation of the air ratio on the anode side. The air ratio provides a measure for the inlet flow rate of air in relation to the rate of reaction. It is defined as the ratio between the number of moles of O_2 contained in the inlet air flow to that produced in the unit cell, per unit time. Assuming that a minimum of 50 mol% N_2 in the anode streams at the stack outlet is required to limit the corrosion of metallic components and that energy costs arising from the supply of air must be limited, the air ratio is allowed to vary between 0.4 and 14 [11]. The mathematical expression for the air ratio is shown in Eq. (28).

$$\psi = \frac{2Ff_{A,O_2}^0(0)}{jLW\nu_{O_2}}. \quad (28)$$

3 Transient response of the SOEC stack: results and discussions

The model described in Section 2 is employed to investigate the stack response during step changes in the average current density. Simulations are performed with fixed and variable air flow rates for temperature control to estimate the stack behaviour.

The system of partial differential and algebraic equations is solved via the finite difference method using gPROMS Model Builder 3.1.4. Parameters such as cell geometry, material properties, thermal properties and operating conditions need to be specified as model input. The model input parameters and operating conditions that are specified are shown in Table 2. The parameters in Table 1 reflect the cell geometry and material properties of an electrolyte-supported cell, different from those of the conventional cathode-supported cell¹⁾ [8–10]. Note that a total stack length of 0.4 m (in the z direction) is assumed, comprising repeating individual cells in series, each of 0.1 m × 0.1 m (in the x and y directions). For this investigation, the inlet gas is kept as 90 mol % H_2O / 10 mol % H_2 .

1) Cai Q, Luna-Ortiz E, Adjiman C S, Brandon N P. The effects of operating conditions on the performance of a solid oxide steam electrolyser: a model-based study. Submitted to Fuel Cells, 2010

Table 2 Model input parameters and operating conditions

input parameters		operating conditions	
h_C/m	0.001	$c_{p,s}/(\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1})$	500
h_A/m	0.001	$c_{p,l}/(\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1})$	500
h_S/m	2.15×10^{-4}	$\lambda_s/(\text{J}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1})$	2
h_I/m	5.00×10^{-4}	$\lambda_l/(\text{J}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1})$	25
L/m	0.4	$\rho_s/\text{kg}\cdot\text{m}^{-3}$	4873
W/m	0.1	$\rho_l/\text{kg}\cdot\text{m}^{-3}$	7800
$\tau_{\text{cathode}}/\text{m}$	5.5×10^{-5}	Nu_C	3.68
$\tau_{\text{electrolyte}}/\text{m}$	9.0×10^{-5}	Nu_A	3.68
$\tau_{\text{anode}}/\text{m}$	7.0×10^{-5}	α	0.5
$\sigma_{\text{cathode}}/(\Omega^{-1}\cdot\text{m}^{-1})$	1.0×10^5	T_C^0/K	1073
$\sigma_{\text{electrolyte}}/(\Omega^{-1}\cdot\text{m}^{-1})$	1.9	cathode stream inlet composition	10mol% H_2 /90mol% H_2O
$\sigma_{\text{anode}}/(\Omega^{-1}\cdot\text{m}^{-1})$	1.0×10^4	anode stream composition	79mol% N_2 /21mol% O_2
$D_{\text{eff,cathode}}/(\text{m}^2\cdot\text{s}^{-1})$	8.5×10^{-5}	operating pressure/MPa	0.1
$D_{\text{eff,anode}}/(\text{m}^2\cdot\text{s}^{-1})$	14.5×10^{-6}	initial average current density $/(A\cdot\text{cm}^{-2})$	1.0
ε_S	0.4	steam utilisation factor/%	80
ε_I	0.7		

The addition of 10 mol % H_2 in the cathode inlet stream is assumed sufficient to avoid the oxidation of the materials at elevated temperature. The steam utilisation factor, i.e. the percentage of the total inlet steam flow rate that is consumed by the reaction, must also be set. A higher steam utilisation factor corresponds to a higher H_2 production rate for a given amount of steam and is therefore desirable. However, it is also important for the steam utilisation factor to be low enough to avoid a significant increase in the cathode concentration overpotential caused by steam starvation near the cell outlet. Here, a value of 80% is chosen. The stack is initially operating with an inlet cathode gas temperature of 1073 K and at an average current density of 1.0 A/cm^2 . The effects of step changes in the average current density from 1.0 A/cm^2 to 0.75, 0.5 and 0.2 A/cm^2 are investigated. The step change in the average current density is taken to happen instantly.

Steady-state simulations without air flow at the anode stream are first carried out to predict the cell potential and the temperature distribution in the stack under a range of potential operating conditions, providing a base case for cell behaviour. The cell potentials at different current densities are shown in Fig. 2. It can be seen that the cell potential increases with increasing average current density at 1073 K. The temperature distribution along the cathode for cell operation at average current densities of 1.0, 0.75, 0.5 and 0.2 A/cm^2 , maintaining all other conditions consistent with Table 1, are shown in Fig. 3. The inlet temperature is fixed at 1073 K. Note that the cathode stream temperature changes rapidly after the cell entry, reaching the temperature of other cell components within a very short distance of the inlet. While the temperature

Fig. 2 Cell potential as a function of average current density at 1073 K

increases along the cell at 1.0, 0.75 and 0.5 A/cm^2 , featuring exothermic operation, the temperature decreases along the cell at 0.2 A/cm^2 , featuring an endothermic operation. As can be seen in Fig. 3, the overall temperature gradient (i.e. the difference between the outlet temperature and the inlet temperature) depends significantly on the average current density; a temperature gradient of 479 K is found for operating at 1.0 A/cm^2 , 292 K for 0.75 A/cm^2 , 120 K for 0.5 A/cm^2 and 50 K for 0.2 A/cm^2 . Previous work has indicated that the maximum allowable total temperature difference along a 0.1 m cell is 100 K [11], otherwise the cell is at the risk of breakdown. As temperature gradients of above 100 K are observed along the 0.1 m cell at most of the investigated current densities,

Fig. 3 Cathode stream temperature along the cell at different average current densities

strict cell temperature control is required to avoid significant thermal excursion.

The effect of feeding air on the anode side on the cell

temperature profiles is investigated in further steady-state simulations, using an appropriate air ratio. The air ratios required to maintain an acceptable overall temperature gradient for different average current densities are obtained. The cathode stream temperature profiles along the cell are shown in Fig. 4, comparing the two cases with and without air flow at the anode stream. As shown in Fig. 4(a)–(c), an air ratio of 12.35, 5.92 and 0.73 is used respectively for operating at 1.0, 0.75 and 0.5 A/cm² to keep the temperature gradient within acceptable limits. The air ratio is chosen for each case so as to obtain a temperature difference of 70 K between the inlet and the outlet, which is much lower than the maximum allowable total temperature difference of 100 K. For the case of operating at 0.2 A/cm², there is no need to use air flow at the anode stream for temperature control as the absolute temperature difference between the inlet and the outlet is just 50 K, as can be seen from Fig. 3. The stack is under endothermic operation in this case.

The stack is expected to have thermal excursions when changing the current density from its initial operating value of 1.0 to 0.75, 0.5 and 0.2 A/cm². Temperature control is

Fig. 4 Cathode stream temperature along the cell for an inlet temperature of 1073 K
(a) At current density of 1.0 A/cm², (b) at current density of 0.75 A/cm², (c) at current density of 0.5 A/cm²

thus required to maintain the temperature at its set-point and to minimise the temperature changes during a step change in the current density. The results of dynamic simulations are presented for the open-loop case in which the stack temperature is left uncontrolled as well as for the closed-loop case in which an attempt has been made to provide temperature control. In the former, the air ratio is maintained constant at 12.35, the air ratio used when operating at 1.0 A/cm^2 , while in the latter, it is adjusted progressively until it reaches the air ratio corresponding to the required steady-state air ratio at new current density, as shown in Fig. 4. The air ratio is changed linearly over a period of 100 s, as illustrated in Fig. 5. Note that the change in air ratio is purposefully selected to be rather slow here such that its effects on the stack temperature would clearly appear. As shown in Fig. 5, the air ratio is adjusted from 12.35 to 5.92 and 0.73 respectively when the current density is changed from 1.0 to 0.75 and 0.5 A/cm^2 . It has been discussed before that there is no need for temperature control when operating at 0.2 A/cm^2 as the absolute overall temperature gradient along the cell length is within the temperature gradient limit. Whereas, when the stack switches from operating at 1.0 to 0.2 A/cm^2 , the stack is switching from the exothermic operation mode to the endothermic operation mode; the stack will go through a sudden temperature change across the stack. It is thus desirable to investigate the possibility of minimising the temperature change during such a step change in the average current density. The recommended maximum value of air ratio (i.e. 14) and other higher values have been used to see their effect on the temperature change. It is clear from our investigation that a sudden temperature drop still exists even with high air ratio values such as 17, and it is impossible to change the operation from endothermic to exothermic by manipulating air ratio. Furthermore, air ratio values higher than 14 have similar stack behaviour to that with an air ratio of 14. Thus only the case of changing air ratio from 12.35 to 14 is shown for the step change in current density from 1.0 to 0.2 A/cm^2 , as is seen in Fig. 6.

The transient response of the cathode stream outlet temperature during step changes in the average current density is shown in Fig. 6, with and without air ratio manipulation. In Fig. 6, a rapid fall in the outlet temperature is observed soon (within 200 seconds) after the step changes from 1.0 to 0.75, 0.5 and 0.2 A/cm^2 , when there is no air ratio manipulation, i.e. when the air ratio is kept constant in spite of the step changes. The rapid fall of the temperature visible in Figs. 6 (a), (b) and (c) is attributed to the instantaneous change in the current density. The decrease in the average current density causes a decrease in the heat generated via irreversible losses, reducing the stack temperature. The minimum outlet temperature of around 1116, 1089 and 1055 K is reached following the step decrease in the average current density from 1.0 to 0.75, 0.5 and 0.2 A/cm^2 respectively, when there is no air ratio manipulation, i.e. when the air ratio is

Fig. 5 Changes in the air ratio, applied to the stack in response to step changes in current density

kept at 12.35 which is the control value for 1.0 A/cm^2 . The outlet temperature with air ratio manipulation in Figs. 6 (a) and (b) is characterised by moderate oscillations. Following the manipulation of the air ratio, the outlet temperature is eventually returned to its initial value after a decrease. After a negative step change in the average current density, the decrease in the air ratio results in decreased convective cooling of the stack, causing the stack temperature to rise back up to the initial value. When the average current density is changed from 1.0 to 0.75 A/cm^2 , the outlet temperature takes 540 seconds (9 minutes) to return to the initial value, as shown in Fig. 6 (a); when the average current density is changed from 1.0 to 0.5 A/cm^2 , a longer time (about 1800 seconds, i.e. 30 minutes) is required to stabilize the outlet temperature, as shown in Fig. 6 (b). When the average current density is changed from 1.0 to 0.2 A/cm^2 , the outlet temperature can not be returned to its initial value, even with the air ratio being manipulated from its initial value of 12.35 to a maximum value of 14, as shown in Fig. 6 (c). In this case, a minimum temperature of about 1057 K is reached after 490 seconds (7 minutes). The transient responses of the stack with air ratio manipulation are further compared in Fig. 7 for the three cases of switching the operating current density from 1.0 to 0.75, 0.5 and 0.2 A/cm^2 respectively. It is clear that a small step change in the current density (e.g. from 1.0 to 0.75 A/cm^2) causes small temperature change and requires a short time to bring the temperature back to its initial value; a doubling in the decrease in the current density (e.g. by going from 1.0 to 0.5 A/cm^2) results in disproportionately large temperature change and time to bring the temperature back. When the step change in the current density is too big (e.g. from 1.0 to 0.2 A/cm^2) in which case the operating mode changes from exothermic to endothermic, the application of the temperature controller by manipulating air ratio at the anode side can not bring the temperature back.

Fig. 6 Transient response of the cathode stream outlet temperature during step changes in current density
(a) From 1.0 to 0.75 A/cm², (b) from 1.0 to 0.5 A/cm² and (c) from 1.0 to 0.2 A/cm²

Fig. 7 Comparison of the transient response of the cathode stream outlet temperature

The transient response of the maximum localized temperature gradient in the solid structure for the imposed changes in the current density, in open- and closed cases (i. e. with and without air ratio manipulation), is presented in Figs. 8 and 9. In all the cases, the maximum localized solid

structure temperature gradient is below 10 K/cm which is the maximum allowed localized solid structure temperature gradient, indicating that the stack is under safe operation. A high maximum localized temperature gradient of 9.6 10 K/cm is observed for operation at 1.0 A/cm², just below the limit condition of 10 K/cm. When the current density is decreased to 0.75, 0.5 and 0.2 A/cm², the observed maximum temperature gradient is lowered. For the cases with air ratio kept constant at 12.35, as shown in Fig. 8, the maximum solid structure temperature gradient is observed to have some small oscillation and then reach 5.3, 1.6 and 1.1 K/cm respectively for changes in the current density from 1.0 to 0.75, 0.5 and 0.2 A/cm². For the cases with air ratio manipulation, as shown in Fig. 9, the maximum solid structure temperature gradient is observed to have small oscillation for changing the current density from 1.0 to 0.75 and 0.2 A/cm² but large oscillations for changing the current density from 1.0 to 0.5 A/cm²; the stabilized maximum solid structure temperature gradient is observed to be 5.1, 3.5 and 1.0 K/cm respectively for changing the current density from 1.0 to 0.75, 0.5 and 0.2 A/cm².

The transient response of the cell potential during step changes in the average current density, imposed with and

Fig. 8 Transient response of the maximum localized solid structure temperature gradient in open-loop cases

Fig. 9 Transient response of the maximum solid structure temperature gradient in closed-loop cases

without air ratio manipulation, is shown in Figs. 10 and 11. During a negative step change, the cell potential is instantaneously decreased due to an immediate fall in irreversible losses. The stack temperature, on the other hand, is reduced over a greater time interval as shown in Fig. 6. Such a reduction in the stack temperature causes the irreversible losses to progressively rise, increasing the cell potential until the final steady state is reached. Without air ratio manipulation, the negative step change to 0.75, 0.5 and 0.2 A/cm² leads to minimum cell potentials of around 1.47, 1.32 and 1.11 V respectively, as shown in Fig. 10; in the cases with air ratio manipulation, the step change to 0.75, 0.5 and 0.2 A/cm² causes minimum cell potentials of around 1.45, 1.29 and 1.108 V respectively, as shown in Fig. 11. Compared to the cell potentials predicted by the steady state simulations in which there is no air flow in the anode stream, the cell potentials shown in Figs. 10 and 11 are higher for 1.0, 0.75 and 0.5 A/cm², but lower for

Fig. 10 Transient response of the cell potential in open-loop cases

Fig. 11 Transient response of the cell potential in closed-loop cases

0.2 A/cm². This is mainly due to the effect of temperature control. With air flow in the anode stream, the temperatures are reduced in the cases of operation at 1.0, 0.75 and 0.5 A/cm², but increased in the case of operation at 0.2 A/cm². Thus the cell potential is increased and decreased accordingly.

It takes up to 300 seconds for the cell potential to stabilize itself in the cases without air ratio manipulation; a longer time of around 600 seconds is needed for the cases with air ratio manipulation. The differences between Figs. 10 and 11 are mainly attributed to the differences in the temperature profiles. As shown in Fig. 6, upon the change of the current density from 1.0 to 0.75, 0.5 and 0.2 A/cm², the outlet temperatures are higher in the cases with air ratio manipulation than those without air ratio manipulation. On the other hand, the temperature profiles in the cases with air ratio manipulation are characterised by oscillations and a longer period of stabilization. Thus the cell potentials in Fig. 11 are marginally lower and take a longer time to stabilize, compared to those in Fig. 10.

4 Conclusions

A one-dimensional dynamic model of a planar SOEC stack has been employed to study the dynamic behaviour of such an SOEC and the prospect for stack temperature control through variation of the air flow rate. Step changes in the average current density are imposed to the stacks, replicating the situation in which the changes in the supply of input electrical energy are experienced, for example from a renewable supply, or the sudden switch-off of the stack. Such simulations have been performed both with and without the manipulation of the air ratio, providing some insight into the potential for temperature control.

The stack temperature and cell voltage are altered by the step changes in the average current density. Without the variation of the air flow rate, a sudden fall in temperature (within 200 seconds) is observed during all the step changes in the average current density. The interim temperature excursions between the initial and final steady states are observed to be reduced by the introduction of air ratio changes. The use of the air ratio as a control variable ensures the maximum overall temperature gradient and the maximum localized temperature gradient in the solid structure remain within acceptable bounds for some small to medium changes in the average current density, but not for large changes. The smaller step changes in the average current density are more easily handled in that a considerably shorter time is required to return to the initial temperature. For example, for a step change from 1.0 to 0.75 A/cm², the stack takes 9 minutes to adjust the temperature back to its initial temperature; whilst for a step change from 1.0 to 0.5 A/cm², the stack takes 30 minutes to do the temperature adjustment. When the step change in the average current density is too big (e.g. from 1.0 to 0.2 A/cm²), altering the stack from a typical exothermic mode to an endothermic mode, a large drop in the temperature occurs and a simple manipulation of the air ratio is insufficient to bring the temperature back to its initial value. Note that the stack goes through a temperature drop of around 88 K over the period of 300 seconds, when the current density is decreased suddenly from 1.0 to 0.2 A/cm² in both cases with and without air ratio manipulation, as shown in Fig. 6. If the stack could survive the temperature drop of 88 K over the period of 300 seconds, such shut-down may not be destructive to the stack, given that the maximum solid structure temperature gradient is small and stabilizes at 1.0 K/cm. The control of stack temperature is observed to decrease the difference between the cell potential at the initial steady state and that at the final steady state, compared to the case without the control. The cell potential transitions take a longer time to reach the final steady state when a temperature controller via the variation of the air flow rate is employed.

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Notation

$c_{p,C}, c_{p,A}, c_{p,S}, c_{p,I}$	heat capacity of the cathode and anode gas streams, solid structure and interconnect/(J·kg ⁻¹ ·K ⁻¹)
$C_{H_2}, C_{H_2O}, C_{O_2}, C_{N_2}$	concentration of hydrogen, steam, oxygen and nitrogen in the cathode and anode gas streams/(mol·m ⁻³)
C_i	concentration of gas species i in the cathode and anode gas streams/(mol·m ⁻³)
C_i^0	concentration of gas species i at the cell inlet/(mol·m ⁻³)
$C_{H_2}^{TPB}, C_{H_2O}^{TPB}, C_{O_2}^{TPB}$	concentration of hydrogen, steam and oxygen at the triple phase boundary/(mol·m ⁻³)
$d_{h,C}, d_{h,A}$	hydraulic diameter of the cathode and anode gas channels/m
$D_{eff,cathode}, D_{eff,anode}$	average effective diffusivity coefficient of the cathode and anode/(m ² ·s ⁻¹)
$E_{cathode}, E_{anode}$	activation energy for the exchange current density of the cathode and anode/(J·mol ⁻¹)
$E_{electrode}$	activation energy for the exchange current density of an electrode/(J·mol ⁻¹)
J_A	inlet flow rate of the anode streams/(mol·s ⁻¹)
F	Faraday's constant/(C·mol ⁻¹)
h_C, h_A, h_S, h_I	height of the cathode and anode channels, and thickness of the solid structure and interconnect/m
j	local current density/(A·m ⁻²)
$j_{0,cathode}, j_{0,anode}$	exchange current density of the cathode and anode/(A·m ⁻²)
$j_{0,electrode}$	exchange current density of an electrode/(A·m ⁻²)
$\bar{j}$	Average current density of an electrode/(A·m ⁻²)
k_C, k_A	convective heat transfer coefficient between the solid parts of the cell and the cathode and anode gas streams/(J·m ⁻² ·s ⁻¹ ·K ⁻¹)
$k_{cathode}, k_{anode}$	pre-exponential factor for the exchange current density of the cathode and anode/(Ω ⁻¹ ·m ⁻²)
$k_{electrode}$	pre-exponential factor for the exchange current density of an electrode/(Ω ⁻¹ ·m ⁻²)
L	cell length/m
Nu_C, Nu_A	Nusselt number of the cathode and anode gas streams
P_{O_2}	oxygen pressure in the anode gas stream/Pa
$P_{O_2}^{TPB}$	oxygen pressure at the triple phase boundary/Pa
R	reaction rate (mol·s ⁻¹ ·m ⁻²)
R_{Ohm}	total resistance of the cell including electric and ionic resistances/(Ω·m ²)
$\mathcal{R}$	gas constant (J·mol ⁻¹ ·K ⁻¹)
t	Time/s
T	temperature/K
T_C, T_A, T_S, T_I	temperature of the cathode and anode gas streams, solid structure and interconnect/K

(Continued)

$c_{p,C}, c_{p,A}, c_{p,S}, c_{p,I}$	heat capacity of the cathode and anode gas streams, solid structure and interconnect/(J·kg ⁻¹ ·K ⁻¹)
T_C^0	temperature of the cathode gas stream at the inlet/K
u_C, u_A	velocity of the cathode and anode gas streams/(m·s ⁻¹)
U	cell potential/V
U^0	standard potential/V
U^{rev}	reversible potential/V
$U^{\text{rev,TPB}}$	reversible potential estimated for the gas concentrations at the triple phase boundary/V
W	cell width/m
x	axial coordinate/m
y_{O_2}	mole fraction of oxygen in the anode gas streams
α	transfer coefficient
$\varepsilon_S, \varepsilon_I$	emissivity of the solid structure and interconnect
$\eta_{\text{act,cathode}}, \eta_{\text{act,anode}}$	activation overpotential losses at the cathode and anode/V
η_{conc}	total concentration overpotential losses/V
$\eta_{\text{conc,cathode}}, \eta_{\text{conc,anode}}$	concentration overpotential losses at the cathode and anode/V
η_{Ohm}	Ohmic losses/V
η_{total}	total irreversible losses/V
$\lambda_C, \lambda_A, \lambda_S, \lambda_I$	thermal conductivity of the cathode and anode gas streams, solid structure and interconnect/(J·m ⁻¹ ·s ⁻¹ ·K ⁻¹)
ν_i	stoichiometric coefficient of gas species i
ν_{O_2}	stoichiometric coefficient of gas species i
$\rho_C, \rho_A, \rho_S, \rho_I$	density of the cathode and anode gas streams, solid structure and interconnect/(kg·m ⁻³)
σ	Stefan-Boltzmann constant/(W·m ⁻² ·K ⁻⁴)
$\sigma_{\text{cathode}}, \sigma_{\text{anode}}$	electric conductivity of the cathode and anode/(Ω^{-1} ·m ⁻¹)
$\sigma_{\text{electrolyte}}$	ionic conductivity of the electrolyte/(Ω^{-1} ·m ⁻¹)
$\tau_{\text{cathode}}, \tau_{\text{electrolyte}}, \tau_{\text{anode}}$	thickness of the cathode, electrolyte and anode/m
ψ	air ratio

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