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Dynamic modeling and parameter analysis study on reversible solid oxide cells during mode switching transient processes

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GRAPHICAL ABSTRACT

Reversible solid oxide cells mode switching between electrolysis and fuel cell operation

ABSTRACT

Reversible solid-oxide cells (SOCs) are a promising technology for mitigating the fluctuation of power from renewable sources. Mode switching between electrolysis and fuel cells occurs frequently and is necessary for an SOC stack. Herein, a dynamic SOC-stack model was developed and validated against experimental data. Subsequently, we extensively studied the stack temperature (T_s), voltage (V_s), and reversible efficiency (η_{re}) with different designing and operating parameters, including stack heat capacity (C_s), inlet hydrogen fraction (x_{H_2}), stack operational pressure (p), inlet work medium temperature (T_{in}), current density (I), and mode switching frequency (f). For an actual SOC plant, the stack may work in a nearly adiabatic environment. Our calculation results show that with x_{H_2} increasing from 0.2 to 0.6, the variation in ΔT_s decreases by 25%, V_s increases by 10%, and η_{re} increases by 2.9%. With fourfold increasing in C_s and p , ΔT_s decreases by 75% and 25% and η_{re} increases by 0.47% and 1.8%, respectively, whereas, V_s is nearly unaffected. ΔT_s and ΔV_s almost proportionally increase with I . In relation to T_{in} or f , ΔT_s is unaffected,

ΔV_s decreases, and η_{re} slightly increases. Overall, this work identified the most critical stack designing and operating factors affecting the transient behavior of an SOC stack during mode switching processes. The results can serve as guidelines for SOC-stack design and operation-strategy optimization.

Keywords: Solid-oxide cell; Dynamic stack modeling; Energy storage; Mode switching operation; Transient operation; Reversible efficiency.

1 Introduction

To become independent of fossil fuels and protect the environment adequately, an increasing number of countries encourage the development of Renewable Energy Sources (RES) fueled power plants in recent years [1]. For example, Germany aims to increase the share of renewables to at least 80% of gross power consumption by 2050 [2], and Denmark has an ambitious goal of providing electricity and heat all from renewables by 2035 and realizing a fossil-free energy system by 2050 [3]. Power generated from RES, such as wind, solar, geothermal, and tidal resources, is intermittent or periodical and is often constrained by geography[4, 5]. To overcome these drawbacks, we need to develop electricity energy storage methods [6-8]. The reversible SOC plant is a promising approach to alleviate the unpredictability of power output from RES. Solid oxide cells attract many researchers to focus on their energy-conversion performances [9-11]. SOC plants can work in electrolysis mode to consume the excess electricity generated from RES to produce hydrogen (or carbon monoxide) and oxygen [12]. When power generation is in demand, SOC plants can work in the fuel cell mode to convert the stored fuel to electricity and heat. The reversible SOC stack is the core of the SOC plant [13]. Variations in stack performance during transient processes greatly influence energy storage and conversion efficiency. The temperature and voltage of the stack vary during mode switching. This process may further affect the degradation and lifetime of the stack. To uncover the energy-conversion process in SOC stacks and the operating factors of the stack boundaries control, researchers should consider dynamic stack modeling and parameter sensitive analysis.

Dynamic modeling is a cost-economic and effective way for exploring the transient behavior in research and industrial applications [14, 15]. Many researchers pursued dynamic modeling of the SOC at different levels from a single repeating unit to a stack, and further to a standalone reversible system or integrated with other types of power plants. Considering the dynamic stack model, models at different dimensions were developed. An overview table summarizing the previous modeling efforts on reversible SOC or SOFC can be found in the paper by Bao et al. [16]. Extensive work has been done on modeling reversible SOCs. Hauck et al. [17] established a dynamic model based on Aspen Plus software. They concluded that the overall cell performance can be improved by increasing the

operating pressure or temperature. Based on a 1D transient reversible SOC model, Srikanth et al. [18] proposed a strategy for the optimization of inlet work medium temperature to reduce the temperature variation rate during mode switching transient processes. Zheng et al. [19] presented a 1D dynamic model of a tubular SOC in radius direction. Based on the 1D model, the performance of the SOC during mode switching in the adiabatic environment was studied under step and continuous voltage variation. Ni [20] presented a 2D model to describe the thermal, electrochemical, reversible water gas shift reaction, and methanation reactions in SOCs [21]. Efforts have also been devoted to modeling solid oxide fuel cells (SOFC). Bhattacharyya et al. [22] studied the dynamic characteristics of the tubular SOFC. Salogni and Colonna [13] presented the development and validation of a nonlinear dynamic lumped model of a SOFC stack. Nikooyeh et al. [23] developed a 3D planar model of an internal reforming SOFC stack with a co-flow configuration. The distribution of both temperature and gas composition through the gas channels and stack frames has been studied. Peksen et al. [24] elucidated a 3D thermo-mechanical analysis of a planar SOFC short stack over an entire thermal cycle. Chen et al. [25] presented a 2D thermal model of ethanol-fueled SOFCs and investigated the effects of stack operation conditions on carbon deposition and those of fuel inlet temperature on stack voltage. Some dynamic models have been developed from governing equations and numerical methods [13, 23-25]. Some of the complicated models were developed based on (Computational Fluid Dynamic) CFD software, such as FLUENT and COMSOL Multiphysics[26-30]. Qu et al. [26] developed a 3D dynamic model by using FLUENT. Their modeling results show that the geometry of the oxygen electrode side gas channel has a substantial effect on the oxygen distribution and thus on the overall cell performance. Al-Masri et al. [27] developed a 3D CFD model to predict the thermal performance of a planar SOFC stack and analyzed thermal stress under different operating conditions. Zhang et al. [28] developed a 3D model and studied the influence of different flow configurations (co-, counter- and cross-flow). Nerat and Juričić [29] developed a 3D model by using COMSOL Multiphysics. They identified the current density and inlet velocity of fuel gas as the key parameters for improving fuel utilization and conversion efficiency. Nishida et al. [30] presented an SOFC stack model with combined gas transport and electrochemistry. By using this model, they predicted performance of a stack tested in a furnace or used for in-field power generation.

Several studies have been devoted to SOC system modeling and configuration optimization [31, 32]. Cheng et al. [31] investigated 10 kW-scale SOFC-based systems. Four representative systems are compared in terms of their technical and exergoeconomic performance under identical net power output. Their work provides a theoretical foundation for the design, analysis, and application of SOFC systems. Safari et al. [32] presented a mathematical model of SOFC to simulate dynamic processes and damp low frequency oscillations by control optimization. Perna

et al. [33] modeled a SOFC/MGT hybrid power plant for CHP and analyzed the effect of operation parameters.

The stack durability is another important factor for the SOC technology development. The stack durability under different operating conditions have been extensively studied to clarify the degradation mechanisms involved and counteract the degradation processes. Modeling efforts were also devoted to this area. Navasa et al. [34] developed a 3D multiphysics model of an SOEC cell to reveal the degradation process and explore the boundary conditions aimed at extending stack lifetime. Liu et al. [35] developed a mathematical model to estimate thermal stresses and predict cell lifetime.

At the system level, for standalone SOFC power systems or hybrid power systems, the modeling efforts focus on the optimization of system configuration or control strategies. Wen et al. [36, 37] developed an SOFC model and optimized the design and operational parameters to maximize the power output in steady-state work conditions. Li et al. [38] proposed a model predictive control strategy based on genetic optimization to meet the requirement for the desired fuel utilization and overcome the nonlinear predictive control constraints of the SOFC. Bang-Møller et al. [39] optimized a hybrid CHP plant via exergy analysis. Based on genetic algorithm, Habibollahzade et al. [40] optimized a hybrid SOC system considering the exergy efficiency, total product cost, levelized emissions, and hydrogen production rate. The control of the conditions for mode switching is another research focus. Jin and Xue [41] investigated the transient behavior of SOCs during mode switching in the current density range of -0.16 A cm^{-2} to 0.17 A cm^{-2} . Christopher et al. [42] analyzed the design and techno-economic aspects of reversible SOC systems for distributed energy storage.

Extensive work has been conducted on modeling SOCs with different dimensions from 0D to 3D according to the different research targets. However, most of the previously developed models are validated with experimental data obtained under steady state work conditions. For a dynamic stack, the model should also be validated for the mode switching processes. Previous efforts were devoted primarily to durability studies and optimization of operating parameters under steady-state work conditions. Studies on mode switching transient processes are rather limited. Accordingly, in the current work, a dynamic model of a reversible SOC stack was established and validated with experimental data obtained during mode switching transient processes. An adiabatic work environment was adopted for the stack. The influence of stack design and operation conditions on the stack performance (stack-temperature variation, power output, and efficiency) was studied in detail.

The present work is organized as follows. First, the dynamic model of the reversible SOC stack is presented and validated (Section 2), and the thermal analysis method of the stack during mode switching transient processes is presented (Section 3). Then, the influences of stack design and operation conditions on transient behavior are

investigated (Section 4). The stack temperature, power output, and reversible efficiency during transient processes are discussed in detail (Section 5). Finally, concluding remarks are presented in Section 5. The current work provides new insights into the strategies to improve the efficiency and extend the lifetime of reversible SOC stacks.

2 Dynamic modeling of a reversible SOC stack

The dynamic model of an SOC stack includes a thermodynamic sub-model and an electrochemical sub-model, which are coupled together. In the fuel cell mode, SOC converts chemical energy into electricity and heat, whereas in electrolysis mode, it converts electricity and heat into chemical energy. The thermal states of the SOC affect electrochemistry and energy-conversion efficiency, and electrochemistry also influences stack temperature. The coupled relations among the fluid mechanics, thermodynamics, and electrochemistry are illustrated in Fig. 1.

Fig. 1 Process diagram of the dynamic SOC-stack model developed in this work

For the dynamic model developed in this work, the following simplifications and assumptions were adopted:

- (a) The work fluids are homogeneous and continuous;
- (b) The lump parameter method is adopted for the SOC stack;
- (c) Ideal gas properties are adopted for all the work gases;
- (d) The mass of the stack itself is set as constant;
- (e) The thermal inertia of the stack was primarily due from the solid structure, whereas the thermal inertia of the work medium stored in the stack (i.e., gases) is very low compared with that of the solid structure and hence can be neglected.

2.1 Electrochemical model of the SOC

Electrochemical reactions occur at the three-phases boundaries (TPB), which are basically interfaces formed by the electrocatalyst, electrolyte, and gas-phase boundaries [43]. The output voltage of the SOC can be described by

Eq. (1) [44] as follows:

$$\begin{aligned} V_{\text{cell}} &= E - V_{\text{act}} - V_{\text{ohm}} - V_{\text{diffu}}, \\ V_s &= N \cdot V_{\text{cell}} \end{aligned} \quad (1)$$

where V_{cell} stands for the output voltage of the single cell, V; E signifies the cell thermodynamic voltage (i.e., Nernst Potential), V; V_{act} denotes the cell activation loss, V; V_{ohm} refers to the cell ohmic loss, V; V_{diffu} refers to the cell diffusion loss, V; V_s is the output voltage of the stack, V; and N denotes the number of the single repeating unit.

i. Thermodynamic voltage

The thermodynamic voltage of the single cell is the ideal voltage from the change in Gibbs free energy during the electrochemical reactions [45]. This parameter is defined by the Nernst equation in Eq. (2) as follow:

$$E = -\frac{\Delta G^0}{2F} + \frac{R \cdot T_s}{2F} \ln \left(\frac{p_{\text{H}_2} \sqrt{p_{\text{O}_2}}}{p_{\text{H}_2\text{O}}} \right), \quad (2)$$

$$\Delta G^0 = G_{\text{H}_2\text{O}}^0 - \left(G_{\text{H}_2}^0 + \frac{1}{2} G_{\text{O}_2}^0 \right), \quad (3)$$

where ΔG^0 stands for Gibbs free-energy change of the reaction, J mol⁻¹; F is the Faraday constant, 96 485 C mol⁻¹; R is the universal gas constant, 8.314 J mol⁻¹ K⁻¹; T_s is the reaction temperature, K; and p_{H_2} , p_{O_2} , and $p_{\text{H}_2\text{O}}$ are the partial pressures of hydrogen, oxygen, and steam in bar, respectively.

ii. Activation loss

In this work, the activation losses from both anode and cathode are considered separately. Butler–Volmer equation (BV) is one of the most fundamental relationships in electrochemical kinetics [46]. As shown in Eq. (4), BV describes how the electrical current of an electrode is determined by the electrode potential. For the modeling of SOCs, it is a semi-empirical method for evaluating the activation loss. The term j_0 represents the exchange current density, A cm⁻². The subscript i represents the anode or cathode.

$$j = j_{0,i} \cdot \left(\exp \left(\frac{(1-\beta) F V_{\text{act},i}}{R T_c} \right) - \exp \left(\frac{-\beta F V_{\text{act},i}}{R T_c} \right) \right), \quad (4)$$

β is the symmetry factor, which varies from 0.25 to 0.5. To simplify the expression of the activation loss, we set β to 0.5. $V_{\text{act},i}$ can be reformulated as in Eq. (5) as follows:

$$V_{\text{act},i} = \frac{R \cdot T_c}{F \cdot n_i \cdot \alpha} \sinh^{-1} \left(\frac{j}{2 j_{0,i}} \right), \quad (5)$$

$$j_{0,i} = \gamma_i \exp \left(-\frac{E_{\text{act},i}}{R \cdot T_c} \right), \quad (6)$$

For the total activation loss of the single cell, V_{act} can be formulated as in Eq. (7) as follows:

$$V_{\text{act}} = \frac{R \cdot T_c}{F \cdot n_a \cdot \alpha} \sinh^{-1} \left(\frac{j}{2j_{0,a}} \right) + \frac{R \cdot T_c}{F \cdot n_c \cdot \alpha} \sinh^{-1} \left(\frac{j}{2j_{0,c}} \right), \quad (7)$$

where α is the transfer coefficient; n is the number of transferred electrons during the chemical reaction; j is the current density of the cell, A cm⁻²; γ is the pre-exponential factor, A cm⁻²; and E_{act} is the activation energy, J mol⁻¹.

iii. Ohmic loss

Ohmic loss accounts for the voltage drop due to resistance to charge transport [18], including the electric charge transport and the ionic current of O²⁻ through the electrolyte layer. The resistance due to ions traveling through the electrolyte dominates the total ohmic loss, and the resistance for electrons to travel through the electrodes is neglected in our model [17]. The overpotential due to ohmic loss is a product of current density and the ohmic part of the area specific resistance (ASR_{ohm}) as given by Eq. (8).

$$V_{\text{ohm}} = j \cdot \text{ASR}_{\text{ohm}}, \quad (8)$$

ASR_{ohm} is the total resistance to the charge transport and is calculated using Eq. (9). This parameter is divided into two parts. The first term in Eq. (9) represents the resistance due to the electrolyte, whereas the second term includes the resistance for the rest of the stack components, such as interconnects, current collectors, and protective layers[18]. The conductivity of the second item is a function of temperature, and its electrical resistance is much smaller than that of the electrolyte layer. The second item can be regarded as constant [17].

$$\text{ASR}_{\text{ohmic}} = \frac{\delta_{\text{el}}}{\sigma_{\text{el}}} + r_{\text{sc}}, \quad (9)$$

$$\sigma_{\text{el}} = \sigma_0 \cdot \exp\left(\frac{-E_{\text{act,el}}}{R \cdot T_s}\right), \quad (10)$$

where r_{sc} is the constant term of ohmic resistance for one single repeating unit (SRU) at steady state, excluding the contribution from the cell, Ω cm²; δ_{el} is the thickness of the electrolyte layer, cm; and σ_{el} is the conductivity of the electrolyte material, Ω^{-1} cm⁻¹.

iv. Diffusion loss

Electrochemical reactions occur at the electrolyte–electrode interfaces [18]. The concentration gradient across the electrodes leads to diffusion loss. Different models have been utilized to model the mass transport in SOC reactors, such as Fick's Model, the Stefan–Maxwell Model and the Dusty Gas Model (DGM) [47-49]. Suwanwarangkul et al. compared these three different models [49]. Among these models, the DGM model has the highest accuracy. However, an analytical solution is difficult to obtain when adopting DGM, and it requires a numerical solution for solving differential equations. This characteristics increases computational effort/time and becomes unfavorable, especially

for simulating transient operations [50]. In this work, Fick's model is adopted for simulating gas diffusion. Equation (11) shows that the reversible voltage depends on the reactant and product concentration [7, 17, 18].

$$V_{\text{diffu}} = V_{\text{diffu,fuel}} + V_{\text{diffu,oxygen}}, \quad (11)$$

$$V_{\text{diffu,fuel}} = \frac{R \cdot T_c}{2 \cdot F} \ln \left(\frac{p_{\text{H}_2\text{O,tpb}} \cdot p_{\text{H}_2,\text{bulk}}}{p_{\text{H}_2\text{O,bulk}} \cdot p_{\text{H}_2,\text{tpb}}} \right), \quad (12a)$$

$$V_{\text{diffu,oxygen}} = \frac{R \cdot T_c}{2 \cdot F} \ln \left(\frac{p_{\text{O}_2,\text{bulk}}}{p_{\text{O}_2,\text{tpb}}} \right), \quad (12b)$$

where $p_{i,\text{bulk}}$ and $p_{i,\text{tpb}}$ are the partial pressures of the species in the bulk flow and at TPB, Pa. The partial pressure at the TPB can be obtained using the Fick diffusion law [45] as follows:

$$p_{i,\text{tpb}} = p_{i,\text{bulk}} - \frac{R \cdot T_s \cdot \delta_i \cdot j}{n_i \cdot F \cdot D_{\text{eff},i}}, \quad (13)$$

where $D_{\text{eff},i}$ is the effective diffusion coefficient for species i in the porous electrode, $\text{m}^2 \text{s}^{-1}$, and it is a function of the electrode porosity ε and tortuosity τ . $D_{\text{eff},i}$ can be obtained with the Bruggeman's correction [45], which is expressed as follows:

$$D_{\text{eff},i} = \frac{\varepsilon}{\tau} \frac{D_{\text{Kn},i} \cdot D_{i-j}}{D_{\text{Kn},i} + D_{i-j}}, \quad (14)$$

where $D_{\text{Kn},i}$ and D_{i-j} are the Knudsen and binary diffusion terms, respectively [51]. The Knudsen term describes the diffusion in porous media and can be expressed as follows:

$$D_{\text{Kn},i} = \frac{d_p}{3} \sqrt{\frac{8 \cdot R \cdot T_c}{\pi M_i}}, \quad (15)$$

where d_p is the pore diameter, m; and M_i is the molecular weight of the species, g mol^{-1} . The binary diffusion coefficient D_{i-j} describes the diffusivity of two species within each other. Good agreement between the Fuller's correlation and measurements has been reported in Solheim's report [52]. In this paper, the parameter can be calculated using the Fuller equation, which is expressed as follows:

$$D_{i-j} = \frac{1.43 \cdot 10^{-7} \cdot T_c^{1.75}}{p \cdot \sqrt{\frac{2}{M_i^{-1} + M_j^{-1}} \left(V_{d,i}^{\frac{1}{3}} + V_{d,j}^{\frac{1}{3}} \right)^2}}, \quad (16)$$

where p is the gas pressure, bar; and $V_{d,i}$ and $V_{d,j}$ are the diffusion volumes of the investigated species, m^3 . Their values are provided in Table 1.

Table 1 Diffusion volume of gas species from literature [53]

Gas species	Diffusion volume
H ₂	6.12
N ₂	18.5
O ₂	16.3
H ₂ O	13.1

2.2 Thermodynamic model of the stack

When developing a dynamic stack model, the stack including the cells, interconnects and sealants and the work medium are considered separately.

For the work fluid, a lumped parameter method is adopted to model each control volume. In the control volume for the work medium, the mass and momentum governing equations are expressed in Eqs. (17)–(19).

$$\frac{dM_i}{d\tau} = \dot{m}_{in,i} + \phi \cdot \dot{m}_{chem,i} - \dot{m}_{out,i}, \quad (17a)$$

$$\dot{m}_{chem,i} = \frac{j \cdot N \cdot A_{cell}}{n \cdot F}, \quad (17b)$$

$$R_r \cdot \dot{m}_{out,total}^2 = p_{in} - p_{out}, \quad (18a)$$

$$p_{in,i} \cdot V = M_i \cdot R \cdot T_i, \quad (18b)$$

$$p_{in} = \sum_{i=1}^7 p_{in,i}, \quad (19a)$$

$$\dot{m}_{out,total} = \sum_{i=1}^7 \dot{m}_{out,i}, \quad (19b)$$

where M signifies the total molar quantity of the work fluid, mol; $\dot{m}$ denotes the molar flow rate of the work fluid, mol s⁻¹; j is the current density, A cm⁻²; n is the number of electrons transferred in the electrochemical reaction; τ represents time, s; p_{in} refers to the work fluid pressure, MPa; p_{out} refers to the outlet boundary, MPa; and R_r is the flow resistance coefficient of a gas channel, kg⁻² MPa s². ϕ is the sign for production (+1) or consumption (−1). i from 1 to 7 represent the gas species, namely, H₂, O₂, H₂O, N₂, CH₄, CO, and CO₂ [45]. In the current work, only H₂, O₂, and H₂O are involved.

For the stack frame, the mass remains constant. The energy conservation governing equations are shown in Eq. (20). The terms on the right side of the equal sign are the enthalpy change of the work medium throughout the stack, the heat released or absorbed from chemical reactions, the electrical power generated or consumed by the stack, and the heat absorbed from or released to the environment [54]. We assumed that the work fluid (gas) is the ideal gas and that the work medium enthalpy is a function of temperature only. The physical properties of the work medium are obtained from literature.

$$C_s M_s \frac{dT_c}{d\tau} = \dot{m}_{in,i} \dot{h}_{in,i} - \dot{m}_{out,i} \dot{h}_{out,i} + \phi \cdot \dot{m}_{chem,i} \dot{h}_{out,i} - \dot{W} + \frac{jNA_{cell}}{2F} \cdot \dot{Q}_{react} + \dot{Q}_{ext} + \dot{Q}_{int}, \quad (20)$$

$$\dot{W} = N \cdot V_{cell} \cdot j \cdot A_{cell}, \quad (21)$$

$$\dot{Q}_{ext} = \sigma \cdot (T_f^4 - T_s^4) \cdot A_{sur}, \quad (22)$$

$$\dot{Q}_{int} = j \cdot A_{cell} \cdot (V_{act} + V_{ohm}) - j \cdot A_{cell} \cdot \frac{T_c \cdot \Delta S^0}{2F}, \quad (23)$$

$$\Delta S^0 = \Delta S_{H_2O}^0 - \left(\Delta S_{H_2}^0 + \frac{1}{2} \Delta S_{O_2}^0 \right), \quad (24)$$

where h is the work fluid enthalpy, J mol⁻¹; $\dot{W}$ stands for the power of the reversible SOC, W; $\dot{Q}_{react}$ is the generation heat rate of the reaction for H₂(g) + 0.5O₂(g) = H₂O (g), W mol⁻¹; A_{cell} is the active area of a single cell, cm²; A_{sur} is the surface area of the stack, cm²; σ stands for the Stefan–Boltzmann constant, W m⁻² K⁻⁴, and ΔS^0 is the entropy of the reaction for H₂(g) + 0.5O₂(g) = H₂O (g), W K⁻¹ mol⁻¹.

2.3 Validation of the coupled dynamic model

The coupled dynamic model was validated with experimental stack test data obtained at the Technical University of Denmark [55]. The stack was an 8-cell experimental stack of 2014-design produced by Topsoe Fuel Cell (TOFC). The cells are planar type Nickel/yttria stabilized zirconia (Ni/YSZ) electrode supported cells from the same production batch. Each cell is composed of a Ni/YSZ support and active fuel electrode, an YSZ electrolyte, and a strontium and cobalt co-doped lanthanum ferrite/gadolinia doped ceria oxygen electrode with a barrier layer between the electrolyte and the oxygen electrode. The cells have a footprint of 12×12 cm² with an active area of 87.7 cm². The interconnect (IC) between every two cells was made of Crofer22APU with protective coating on both sides. The experimental stack was operated in a closed furnace. The supplied work gases are H₂O/H₂ (50/50) for fuel electrode and pure O₂ (100 %) for oxygen electrode. To monitor the stack temperature, eight temperature probes (thermocouples) were inserted into the stack end-plates. Voltage probes in contact with the IC plates were used to monitor the voltage over each SRU, including the contributions from the cell, the IC, and the contact between them. The overall stack voltage can be obtained by summing up the eight SRU voltages and the voltages between the stack end-plates (top- or bottom-plate) and the top or bottom SRU. In the current work, the I - V curves at 1073 K (stack temperature), in which H₂O/H₂ (50/50) was fed to the Ni/YSZ electrode compartment, were used to validate the stack model. The average stack temperature and SRU voltage were adopted to validate the coupled dynamic model. Notably, a full-sized Delta stack produced by TOFC at that time included 50 SRUs. In 2014, Topsoe introduced a next-generation stack design Topsoe Stack Platform (TSP). The new design addresses several issues related to the Delta design, such as larger cell active area, lower degradation rates, and improved robustness of the new design. Data

demonstrating the improved performance and robustness of the TSP stack are available [56].

The fitted model parameters for the SOC cell and the stack are summarized in Tables 2 and 3, respectively. The flow rate and temperature of the inlet gases are listed in Table 4. The furnace temperature and the atmospheric pressure (1 atm) were used as the boundary condition. In the experimental stack testing, the steam was produced by burning H_2 and O_2 in a reactor outside the stack. This reaction enthalpy was partly supplied to the stack and partly released to the environment. This part of heat was considered as a source term in the energy governing equation. However, the exact amount is difficult to quantify, resulting in a small difference between the measured and simulated stack temperature as shown later in this paper. Experimental stack testing data with a different way of generating steam is needed to further calibrate the model, and this testing data will be considered in our future work.

Table 2 Fitting parameters of the SOC cell

Parameter	Definition	Value and Unit	References/ notes
r_{sc}	Constant ohmic resistance term	$5.70 \times 10^{-2} / \Omega \cdot \text{cm}^2$	At 1073 K
σ_0	Pre-exponential factor for the ionic conductivity of the electrolyte	$3.33 \times 10^2 / \Omega^{-1} \cdot \text{cm}^{-1}$	[17]
$E_{act, fuel}$	Fuel electrode activation energy	$1.00 \times 10^5 / \text{J mol}^{-1}$	[17]
$E_{act, el}$	Electrolyte activation energy	$8.56 \times 10^4 / \text{J mol}^{-1}$	[17]
$E_{act, oxygen}$	Oxygen electrode activation energy	$1.00 \times 10^5 / \text{J mol}^{-1}$	[17]
δ_{fuel}	Fuel electrode thickness	$1.50 \times 10^{-5} / \text{m}$	[34]
δ_{el}	Electrolyte thickness	$1.50 \times 10^{-5} / \text{m}$	[34]
δ_{oxygen}	Oxygen electrode thickness	$3.00 \times 10^{-5} / \text{m}$	[34]
A_{cell}	Active area of single cell	$8.77 \times 10^1 / \text{cm}^2$	
d_p	Pore diameter	$2.00 \times 10^{-6} / \text{m}$	[17]
γ_{fuel}	Pre-exponential factor	$1.34 \times 10^6 / \text{A cm}^{-2}$	[17]
γ_{oxygen}	Pre-exponential factor	$2.05 \times 10^5 / \text{A cm}^{-2}$	[17]
ε	Electrode porosity	3.00×10^{-1}	[17]
τ	Electrode tortuosity	5.00×10^0	[17]

Table 3 Fitting parameters of the SOC stack

Parameter	Definition	Value and unit
c_s	Average specific heat capacity of the stack	$5.00 \times 10^2 / \text{J kg}^{-1} \text{K}^{-1}$
M_s	Mass of the stack	$3.70 \times 10^1 / \text{kg}$
N	Number of SRU	8.00×10^0
A_{sur}	Surface area of the stack	$7.00 \times 10^{-2} / \text{m}^2$
σ	Stefan-Boltzmann constant	$5.67 \times 10^{-8} / \text{W m}^{-2} \text{K}^{-4}$
R_f	Flow resistance coefficient	$1.00 \times 10^0 / \text{kg}^{-2} \text{MPa s}^2$
T_f	Furnace temperature	$1.033 \times 10^3 / \text{K}$
$T_{s,\text{initial}}$	Initial stack temperature	$1.073 \times 10^3 / \text{K}$

Table 4 Input gases to the experimental stack

	Gas	Flowrate/ sccm cm^{-2}	Inlet temperature/K
Hydrogen electrode side	$\text{H}_2 / \text{H}_2\text{O} (50:50)$	12.44	1033
Oxygen electrode side	O_2	5.70	1033

When the input flow boundaries of the stack model are identical to the experimental data, the key output parameters, such as the stack voltage, power output, and average stack temperature, can be compared with the experimental values. The mode switching between SOFCs and SOECs was modeled and validated with the experimental data (I – V). I – V measurements were performed first in the SOFC mode and then in the SOEC mode. The simulated stack voltage was calculated as eight times of the average SRU voltage, whereas the experimental data used for comparison is the sum of the eight SRU voltages. The current density variation during SOFC–SOEC mode switching is shown in Fig. 2(a). The model output parameters (voltage, power, and temperature) are plotted in Fig. 2(b)–4(d). The deviations in stack voltage and temperature and their relative errors are plotted in Fig. 2(e)–2(f). The experimental data well agrees with the simulated results, indicating the validity of our model. Fig. 2(c) plots the stack power versus time, where the simulation nearly coincides with the experiment. Fig. 2(d) shows the measured and simulated stack temperature curves that have very similar trends and close values. In fuel cell mode, the stack temperature increases monotonically with the current density, as both the fuel cell reaction and ohmic loss release heat. In the electrolysis mode, the electrolysis reaction is endothermic, whereas ohmic loss releases heat. Hence, the

slope of the stack temperature versus current density (or vs. time as in Fig. 2d) is not that steep, as in SOFC mode. For the stack voltage, a maximum deviation of 0.116 V or 1.34 % of the measured stack voltage is observed as shown in Fig. 2(e). This results in a deviation of ~ 2 W in stack power, which is not easily visible in Fig. 2(c). Fig. 2(f) illustrates the deviation of stack temperature, showing a maximum deviation of 7 K or 0.65%.

Fig. 2 Validation of the dynamic SOC-stack model

3 Analysis methodology

3.1 Fuel utilization rate of the stack during mode switching operation

When the reversible SOC stack works in SOFC mode, the utilization rate (u_i) of the gas can be calculated using Eq. (25). The difference between the inlet and outlet flow rates of fuel is utilized by the cell. During the transient process, u_i may be affected by the inlet and outlet fuel flow rates, as well as the current density. The current density of the cell determines the rate of the electrochemical reaction between H_2 and O^{2-} . In the SOFC mode, the fuel utilization is positive, whereas in the SOEC mode, it becomes negative, because H_2 is produced from the electrochemical reactions. In this paper, only the utilization of hydrogen is considered.

$$u_i = \frac{\dot{m}_{in,i} x_{in,i} - \dot{m}_{out,i} x_{out,i}}{\dot{m}_{in,i} x_{in,i}}, \quad (25a)$$

$$x_{out,i} = \frac{M_i}{\sum_{i=1}^7 M_i}, \quad (25b)$$

where $x_{in,i}$ signifies the fraction of the inlet gas species; and $x_{out,i}$ represents the fraction of the outlet gas species.

3.2 Temperature variation rate of the stack during transient processes

For the SOC, when the work medium boundaries and the current density vary, the thermal status of the stack will be affected. The load cycling process and mode switching operations have significant influences on thermal fatigue and even the material's degradation. By modifying Eq. (20), the temperature variation rate $\left(\frac{dT_s}{d\tau}\right)$ of the stack can be obtained directly. For maintaining the long-time operation in SOC, $\left|\left(\frac{dT_s}{d\tau}\right)\right|$ should be kept at a relatively low level. In this study, 1 K min^{-1} was chosen as the criterion for the temperature variation rate of SOC stacks, that is, the upper limit for safe operation [57, 58].

$$\frac{dT_s}{d\tau} = \frac{\dot{m}_{in,i} \dot{h}_{in,i} - \dot{m}_{out,i} \dot{h}_{out,i} + \phi \cdot \dot{m}_{chem,i} \dot{h}_{out,i} - \dot{W} + \frac{jNA_{cell}}{2F} \cdot \dot{Q}_{react} + \dot{Q}_{ext} + \dot{Q}_{int}}{C_s M_s}, \quad (26)$$

3.2.1 Reversible efficiency of the SOC stack during mode switching transient processes

For the evaluation of the energy conversion and storage performance throughout one charge/discharge cycle in the stack, we introduce in this work a term called reversible efficiency (η_{re}). η_{re} is defined as the total electrical energy produced by the stack during fuel cell mode divided by the total electrical energy supplied to the stack in electrolysis mode. As shown in Fig. 3, the SOC works in electrolysis mode for a period of $2T_0$, and then switches to fuel cell mode for another $2T_0$. E_{In} represents the energy consumed in storage mode (SOEC), whereas E_{Out} represents the electrical power produced in the production mode (SOFC). The ratio of E_{Out} and E_{In} represents the reversible efficiency in one mode switching cycle. Notably, during model validation (Section 2.3), the cycle was designed as

SOFC–SOEC in accordance with the experimental I – V data. For the parametric study presented below, the cycle is changed to SOEC–SOFC to accurately mimic the scenario “Power to Gas to Power”. Alternately, SOFC–SOEC cycle may also be relevant in some occasions, but this part is omitted in this study for conciseness. In this work, the reversible efficiency is calculated considering the stack only and excluding the balance of the plant (BOP) components. When taking the BOP components into account, the efficiency of a reversible system can be obtained and the values will be lower than those (reversible efficiency, η_{re}) reported in this work, as the BOP components require additional energy input.

Fig. 3 Mode switching process for an SOC cell stack

$$\eta_{re} = \frac{\int_0^{2T_0} |\dot{W}| d\tau}{\int_{2T_0}^{4T_0} |\dot{W}| d\tau} \times 100\% , \quad (27)$$

where T_0 is a quarter of the mode switching cycle period.

In an actual SOC plant, the furnace does not exist, and the boundaries of the stack can be regarded as adiabatic to the environment (neglecting the heat loss to the environment). In the SOEC mode, stack temperature decreases due to the endothermic reactions, whereas in the SOFC mode, stack temperature increases, because the power generation process is exothermic. In total, after one cycle in the SOC stack, the temperature of the stack will increase, that is, not all the input electrical power can be converted back, and part of this power is released as heat, where $\eta_{re} < 1$. This condition occurs primarily because the heat released in the SOFC mode and the heat absorbed in the SOEC mode do not cancel each other out. In the adiabatic mode, this condition increases the stack temperature because of the net heat generated. A lower net heat generated means less increase in stack temperature after one mode switching cycle and a closer value of η_{re} to 1.

4 Results and discussion

The stack may operate in off-design work conditions due to the electricity demand. A typical switching cycle for the reversible SOC stack is illustrated in Fig. 4. The entire cycle of switching operation between SOEC and SOFC is 40 000 s ($T_0 = 10\,000$ s). In the first half cycle (A–B–C), the stack works in the SOEC mode (the current is negative), whereas in the second half cycle (C–D–E), the stack works in the SOFC mode (the current is positive). The amplitude of the current density (I_{peak}) is 0.25 A cm^{-2} , and the current variation format is a triangular wave. The triangular wave, including the ramp format, is the same as that in the experimental stack testing. The ramping rate is determined by the peak current density (0.25 A cm^{-2}) and the cycle time (40 000 s). Mode switching occurs in a step manner, in which the stack has to switch first from SOEC operation to open current voltage (OCV), and then from OCV to SOFC operation, or vice versa. Theoretically, if the same gas feeds are used for both SOFC and SOEC operations, then the switching from SOEC to OCV and further to SOFC may occur in seconds. However, for minimizing the thermal shock, an appropriate ramping rate choice for current density might be needed.

Fig. 4 Current density of the stack in a switching cycle

The transient performance of the stack depends strongly on the stack designing and operating parameters. A parametric variation study is necessary to explore general trends. The basic stack design parameters and the boundary conditions are listed in Tables 3 and 4. Different from the model validation part, the inlet temperature of the work medium was 1073 K. The following parts present the influences of the inlet boundaries (operational parameters including fuel fraction, inlet gas temperature, operation pressure, current density, and mode switching frequency) and the thermal capacity (design parameter) of the stack throughout the mode switching transient processes. The temperature (T_s), temperature variation rate ($\frac{dT_s}{d\tau}$), voltage (V_s), output power ($\dot{W}$), fuel utilization (u_{H_2}), and

reversible efficiency (η_{re}) of the stack were illustrated and analyzed in detail.

In the actual experimental stack testing [55], the stack was placed inside a thermostatical furnace. As shown in Section 2, during mode switching process, the stack temperature varied up to 10 K. When the stack is placed in an adiabatic environment (as presented in the simulation below), T_s may greatly vary during transient operations.

4.1 Fuel fraction (x_{H_2})

The components of the fuel electrode inlet work medium are hydrogen (H_2) and steam (H_2O), and oxygen is the only gas species fed to the oxygen electrode. For the fuel electrode, the molar ratio of H_2 to H_2O is 50:50 ($x_{H_2}=0.5$) for the basic work condition. To study the influence of fuel gas composition on the stack transient behavior, an extensive parameter study on x_{H_2} from 0.2 to 0.6 (x_{H_2O} varies from 0.8 to 0.4 accordingly) was carried out and the results are presented in this section.

The initial values for T_s and I at the beginning of the cycle are 1073 K and 0 A cm⁻², respectively. As the input parameter, the variation profile of I is illustrated in Fig. 4. The stack undergoes an entire cycle, beginning from SOEC and ending in SOFC with current density following a triangle wave curve. For the model output parameters, the variations in T_s , $\left(\frac{dT_s}{d\tau}\right)$, V_s , $\dot{W}$, u_{H_2} , and η_{re} during the mode switching processes are presented in Figs. 5(a)–5(f). At $x_{H_2} = 0.2$, T_s first decreases from 1073 K to 1046 K and then increases and reaches a maximum of 1086 K at the end of the cycle. The maximum stack-temperature variation (ΔT_s) is approximately 40 K. The profile of $\left(\frac{dT_s}{d\tau}\right)$ is similar to that of I . Due to the electrochemical reaction, the sign of $\left(\frac{dT_s}{d\tau}\right)$ is determined by the current direction. When I is negative, the stack works in SOEC mode, and the electrochemical reaction is endothermic, and vice versa. $\left(\frac{dT_s}{d\tau}\right)$ decreases from 0 to -0.17 K min⁻¹ at the peak current density in the SOEC mode, and then increases to 0.25 K min⁻¹ at the peak current density in SOFC mode, and eventually returns to 0. The maximum $\left|\frac{dT_s}{d\tau}\right|$ is 0.25 K min⁻¹, which is below the suggested safe operation criterion of 1.0 K min⁻¹[58], which is indicated by the two red dashed lines in Fig. 5(b). By changing the electrolysis current density from 0 to -0.25 A cm⁻², the stack voltage V_s increases from 7.3 V to 7.9 V. In the SOFC mode, with current density increasing from 0 to 0.25 A cm⁻², V_s decreases from 7.6 V to 6.5 V. The stack voltage V_s values at 0, $2T_0$, and $4T_0$ are 7.3, 7.4, and 7.2 V, respectively. The difference is caused by the difference in stack temperatures, even though the current density is 0 A cm⁻² in all the three cases. $\dot{W}$ is the product of I , A_{cell} , and V_s , and the profile of $\dot{W}$ is very similar to that of I . According to Eq. (25), u_{H_2} is negative in the SOEC mode and positive in the SOFC mode for steady-state work status, and its evolution over time adopts a

triangle waveform when the stored work medium in the stack is neglected. The smoothness of the u_{H_2} curves indicates its delayed characteristics during transient processes. η_{re} is an index of reversible energy-conversion efficiency for an integrated charging and discharging process with a value of 87.01 % at $x_{H_2} = 0.2$.

With increasing x_{H_2} from 0.2 to 0.6, the maximum stack temperature variation ΔT_s decreases from 40 K to 30 K. The decrease in ΔT_s indicates the decrease in thermal fatigue during mode switching transient processes. This condition is further reflected by the 25% decrease in the maximum value of $\left| \frac{dT_s}{dt} \right|$. The curves of V_s for different x_{H_2} values are nearly parallel. According to Eqs. (1) and (2), V_s depends on the partial pressure of H_2 , O_2 , and H_2O . When I is identical, V_s increases with the increasing in x_{H_2} . The maximum value of ΔV_s during one cycle is 0.6 V at $x_{H_2} = 0.2$, and this difference is more obvious with increasing x_{H_2} . An enlarged part of the $\dot{W}$ curves at the peak current densities are presented in Figs. 5(g) and 5(h). With increasing x_{H_2} from 0.2 to 0.6, the peak power consumption in SOEC mode increases from 175.4 W to 189.2 W, whereas the peak power production in SOFC increases from 143.7 W to 162.4 W. Considering that u_{H_2} has a direct relation with x_{H_2} , the difference in u_{H_2} is obvious. Under different x_{H_2} values, the maximum difference in u_{H_2} is 0.50 when I reaches its peak value. Theoretically, u_{H_2} depends on current density, inlet hydrogen molar fraction, and gas flow. At the same current density, u_{H_2} decreases with increasing x_{H_2} . With x_{H_2} varying from 0.2 to 0.5, η_{re} increases from 87.01% to 89.92%. The maximum value of η_{re} is 89.92% at $x_{H_2} = 0.5$. Further increase in x_{H_2} from 0.5 to 0.6 results in decreasing η_{re} by 0.01%. In conclusion, an inlet hydrogen fraction of 0.5–0.6 leads to the smallest stack-temperature variation and the highest reversible efficiency during the SOEC–SOFC reversible operation. When the ratio of H_2 and H_2O is 50:50, the diffusion voltage loss is the least compared with other work conditions. This may be one of the reasons that the η_{re} reaches the maximum when $x_{H_2} = 0.5$.

Fig. 5 (a) Temperature, (b) temperature variation rate, (c) voltage, (d) power, (e) fuel utilization, (f) reversible efficiency, and (g), (h) enlarged view of $\dot{W}$ of the stack with different x_{H_2}

4.2 Work medium inlet temperature (T_{in})

The inlet temperature of the work medium (T_{in} in Kelvin) affects the thermal status of the stack and the electrochemical reactions. The designed inlet gas temperature is 1073 K in rated work conditions. To explore the allowance and the most suitable T_{in} , four values are selected: 973, 1073, 1173, and 1273 K. The T_s curves under different T_{in} are approximately parallel. For an elaborate description on T_s , the curve of $\left(\frac{dT_s}{d\tau}\right)$ can reflect the detailed variation during transient processes. The trends of variation in $\left(\frac{dT_s}{d\tau}\right)$ for different T_{in} values are similar, and closely follow the variations in I . As shown in Fig. 6(b), the highest $\left|\frac{dT_s}{d\tau}\right|$ is 0.30 K min^{-1} , which appears at $3T_0$ with $T_{in} = 973 \text{ K}$. At identical I , with increasing T_{in} , V_s increases in the SOFC mode but decreases in the SOEC mode. The change in SOEC mode is much higher than that in the SOFC mode. The maximum $|\Delta V_s|$ in one mode switching cycle is 3 V with $T_{in} = 973 \text{ K}$. Increasing T_{in} reduces the stack voltage variation, especially in the SOEC mode. Fig. 8(d) presents the variation of $\dot{W}$ with time under different T_{in} values. The enlarged views at minimum and maximum $\dot{W}$ are presented in Figs. 6(g) and 6(h). The power consumption in the SOEC mode decreases with increasing T_{in} , whereas the power production in SOFC mode increases with increasing T_{in} . The difference in u_{H_2} is minor. The thermal status of the stack affects the stored work medium's thermal states, such as specific volume. Even at the same current density, u_{H_2} differs due to the different amounts of H_2 involved in the electrochemical reactions. The minor difference in u_{H_2} may be due to the molar quantity of the stored work medium that is inversely proportional to T_s . When T_{in} varies from 973 to 1273 K, η_{re} increases from 80.49% to 93.62%, indicating that T_s and T_{in} have great influence on the reversible efficiency of the SOC. Ohmic voltage loss dominates all the voltage losses in SOC cells.

A high operating temperature reduces the electrolyte resistance. According to Equations (8)–(10), with increasing in the cell temperature (T_c), σ_{el} increases and V_{ohm} decreases. In total, when increasing the stack operation temperature (such as rising the gas inlet temperature), the ohmic loss will be reduced both in SOEC and SOFC modes. η_{re} increases accordingly as shown in Fig. 6(f). In reality the choice of operating temperature is limited by several factors, among which the performance and durability of cells, stack components, and stacks are the most important ones. For example, the widely used ferritic stainless-steel interconnects are limited to an operation temperature of 1123 K or lower. At the system level, we should also consider the BOP components and the overall system efficiency.

Fig. 6 (a) Temperature, (b) temperature variation rate, (c) voltage, (d) power, (e) fuel utilization, (f) reversible efficiency, and (g), (h) enlarged view of $\dot{W}$ of the stack with different T_{in}

4.3 Work medium operation pressure (p)

The pressure of the work medium (p) may affect the electrochemical reactions operating in the stack. The operational pressure is set to 0.1 MPa. A parametric study of the operational pressure on stack transient behavior was conducted, and the results are presented in this section. A dimensionless parameter of the stack operational pressure (R_p) was proposed to represent the variation in operational pressure.

$$R_p = \frac{p}{p_0}, \quad (28)$$

where p_0 is the designed operational pressure of the stack (0.1 MPa).

The transient behavior of the stack with different R_p is illustrated in Fig. 7. With increasing R_p , the stack temperature T_s increases slightly in SOEC mode but decreases in SOFC mode. Hence, the stack temperature variation (ΔT_s) reduces. This finding is also observed for $\left| \frac{dT_s}{d\tau} \right|$, as shown in Fig. 7(b). The peak stack voltage in the SOEC mode V_s increases from 8.4 V to 8.7 V with increasing R_p from 1.0 to 4.0. Although increasing R_p can improve V_s , the

improvement in V_s is limited or not distinct, as depicted in Fig. 7(c). According to the governing equation of Eq. (2), by neglecting the influence of T_s , increasing p_{O_2} can increase E , but the improvement is proportional to $\frac{1}{p_{O_2}}$. The curves of $\dot{W}$ with different R_p are nearly in parallel, as shown in Fig. 7(d). The differences at the peak $\dot{W}$ are 5 W in the SOEC mode and 10 W in the SOFC mode, as shown in Figs. 7(g) and 7(h). u_{H_2} is a function of current density alone at fixed amount of gas reactants. However, during the transient process, with increasing R_p , the stored work medium increases, thus decreasing fuel utilization at the same current density and enhancing the delayed characteristics in u_{H_2} . By increasing R_p from 1.0 to 4.0, the peak u_{H_2} reduces by one third both in the SOEC and SOFC modes. In some operation scenarios, u_{H_2} is set as constant. When the current density varies, the inlet flowrate of the gases to the hydrogen electrode needs to be adjusted beforehand to overcome the time lag effects, as shown in Fig. 9e. At fixed gas flowrate, the current density shall be adjusted in advance to maintain u_{H_2} in an acceptable range. With increasing R_p from 1.0 to 4.0, η_{re} increases from 89.92% to 91.72% monotonically. When increasing the operation pressure, V_s is improved both in SOEC and SOFC modes. The decreasing in stack-temperature fluctuation results in less electricity energy that is converted to thermal energy form in one mode switching cycle. In summary, increasing the stack operation pressure reduces stack-temperature variation and hence increases the reversible efficiency of the SOC stacks. However, from a system point of view, increasing pressure may not necessarily increase the system efficiency, because operating at elevated pressure requires additional energy input.

Fig. 7 (a) Temperature, (b) temperature variation rate, (c) voltage, (d) power, (e) fuel utilization, (f) reversible efficiency, and (g), (h) enlarged view of $\dot{W}$ of the stack with different R_p

4.4 Current density amplitude (I_{peak})

For a mode switching process, the allowable current density peak value (I_{peak}) represents the capacity of the

stack power. The starting value of I_{peak} was set to 0.25 A cm^{-2} . A parametric study of I_{peak} was conducted, and the results are presented in this section. A dimensionless parameter of the operational current density (R_I) was proposed as follows:

$$R_I = \frac{I_{\text{peak}}}{I_{\text{peak},0}}, \quad (29)$$

where $I_{\text{peak},0}$ is the value adopted in the experimental stack testing (0.25 A cm^{-2}).

The influence of R_I on the stack transient performance is illustrated in Fig. 8. With increasing R_I from 0.5 to 3.0, ΔT_s proportionally increases from 35 K to 140 K. As shown in Fig. 8(b), $\left| \frac{dT_s}{d\tau} \right|$ increases in proportion to I . The increase in $\left| \frac{dT_s}{d\tau} \right|$ is more pronounced in the SOFC mode than in SOEC mode. At $R_I = 3.0$ and at the peak SOFC current density, $\left| \frac{dT_s}{d\tau} \right|$ reaches the maximum value of 1.02 K min^{-1} , exceeding the upper limit of allowable stack-temperature variation. Our results indicate that for an adiabatic reversible SOC stack, the maximum allowable current density should not exceed 0.75 A cm^{-2} for the type of stack that we investigated here. For the identical I , V_{ohm} increases with increasing R_I proportionally. The increase in R_I causes changes in the molar fraction of the reactants accordingly, and Nernst voltage (E) may be affected directly. Considering the SOFC mode, when R_I increases from 1.0 to 2.0, V_{ohm} will be doubled and E will decrease, as the partial pressure of H_2 decreases and that of H_2O increases. Hence, V_s decreases with increasing R_I as illustrated in Fig. 8(c). The variation of $\dot{W}$ is proportional to the change in R_I . This condition is similar to that of u_{H_2} , as shown in Fig. 8(e). I reaches its peak value at $3T_0$. However, the maximum value of u_{H_2} appears at the time later than $3T_0$. The peak value of u_{H_2} appears at the same time for different R_I , demonstrating that the delay characteristics is affected by the stack volume and slightly affected R_I . With increasing operational current density of the stack, the activation and ohmic voltage losses enhance accordingly. More power is needed in the SOEC mode, and less electricity can be generated in the SOFC mode. Hence, the reversible efficiency η_{re} decreases with increasing R_I . In summary, with increasing the peak current density, the fatigue of the stack due to thermal cycling increases, and the reversibility of the energy-conversion process decreases. For the stack to be protected and for maintaining a high η_{re} during the transient operation in an adiabatic environment, the current density needs to be kept within a reasonable range.

Fig. 8 (a) Temperature, (b) temperature variation rate, (c) voltage, (d) power, (e) fuel utilization, and (f) reversible efficiency of the stack with different R_I

4.5 Mode switching frequency (f)

The operation mode of the stack is determined by the electricity demand. In an actual operational SOC plant, the frequency depends on the grid demand, and it can be varied by simply varying the current density ramping rate. The mode switching frequency may affect the transient behavior heavily. A parametric study on the influence of the mode switching frequency was conducted, and the results are presented here. A dimensionless parameter of mode switching frequency (R_f) was proposed as follows:

$$R_f = \frac{f}{f_0}, \quad (30)$$

where f_0 is the original switching mode frequency adopted in the experimental stack testing, where $f_0 = 2.5 \times 10^{-5}$ Hz (1/40 000 s).

Fig. 9 illustrates the profiles of the model output parameters with different R_f values. With R_f increasing from 1.0 to 4.0, the maximum temperature variation ΔT_s decreases from 15 K to 5 K. However, the peak value of $\left| \frac{dT_s}{d\tau} \right|$ remains the same. This finding shows that the main factor affecting $\left| \frac{dT_s}{d\tau} \right|$ is I . R_f slightly influences the stack voltage. The peak value of V_s decreases from 8.45 V to 8.30 V in the SOEC mode and increases from 7.25 V to 7.4 V in the SOFC mode. With increasing R_f , the direction of the electrochemical reactions revert more frequently. The work medium stored in the stack can be refilled in time. As shown in Fig. 9(e), the fluctuation of u_{H_2} becomes less with increasing R_f . Figs. 9(d) and 9(f) show the plot of the power consumption and generation ($\dot{W}$) during mode switching processes and the reversible efficiency (η_{re}) of the SOC stack with different R_f values. The frequency influences the reversible efficiency indirectly. As shown in Fig. 9 (a), at $4T_0$, the final stack temperature T_s decreases with increasing R_f . The increasing in the mode switching frequency benefits the stack works in a relatively narrow range temperature. The peak values of V_s reduce in the SOEC mode, and the minimum values of V_s increase in the SOFC mode. In other words, for an identical mode switching cycle, the required power for electrolysis reduces and the generated electricity increases. This phenomenon can explain why the reversible efficiency increases with R_f .

Fig. 9 (a) Temperature, (b) temperature variation rate, (c) voltage, (d) power, (e) fuel utilization, and (f) reversible efficiency of the stack with different R_f

4.6 Stack heat capacity (C_s)

The product of the stack specific heat capacity (c_s) and the stack mass (M_s) is the stack heat capacity (C_s). Here, a parametric study on C_s was conducted, and the results are plotted in Fig. 10. A dimensionless parameter of R_{Cs} was introduced as follows:

$$R_{Cs} = \frac{c_s M_s}{c_{s,0} M_{s,0}}, \quad (31)$$

where $c_{s,0}$ and $M_{s,0}$ are the original specific heat capacity and mass of the stack, respectively, as listed in Table 3.

During mode switching transient processes, the stack thermal state may be affected by R_{Cs} . Electrochemical reactions occur in the stack, and T_s greatly influences the physical and chemical properties of the work medium.

With increase in R_{Cs} from 1.0 to 4.0, the maximum stack-temperature variation ΔT_s decreases from 32 to 8 K. The increase in R_{Cs} also reduces $\left| \frac{dT_s}{d\tau} \right|$ significantly. To extend the stack lifetime, increasing R_{Cs} may contribute to alleviating the fatigue due to thermal cycling especially in adiabatic environment. The influence of R_{Cs} on V_s is not significant, as shown in Fig. 10(c). Figs. 10(f) and 10(h) present an enlarged view of $\dot{W}$ at peak values. As depicted

in Fig. 10(e), a slight difference is observed in u_{H_2} with different R_{Cs} values. The stack thermal states are affected by R_{Cs} , thus possibly affecting the molar quantity of the stored work medium in the stack (according to the ideal gas equation). The u_{H_2} value is determined by the difference between the inlet and outlet fuel flow rates (molar quantity of stored gases in the stack). The change in ΔT_s may slightly influence the stored work medium molar quantity. Therefore, the difference in u_{H_2} is negligible. As shown in Fig. 10(c), with the increasing in R_{Cs} from 1.0 to 4.0, V_s decreases obviously in the SOEC mode, and the minimum values are very close for different R_{Cs} values. Results show that less power is needed in electrolysis mode, and the stack can generate nearly identical electricity in the fuel cell mode. This is the mainly reason for η_{re} increasing from 89.92% to 90.39% with R_{Cs} from 1.0 to 4.0. In total, increasing stack heat capacity can reduce the stack temperature variation rate and improve the reversible efficiency of the energy-conversion processes.

Fig. 10 (a) Temperature, (b) temperature variation rate, (c) voltage, (d) power, (e) fuel utilization, (f) reversible efficiency, and (g), (h) enlarged view of $\dot{W}$ of the stack with different R_{Cs}

In this section, we have conducted a detailed parameter study on a number of stack operating and design parameters, including the fuel fraction of the inlet gas, the inlet gas temperature, the stack operation pressure, the current density, the mode switching frequency, and the stack heat capacity. The stack transient performance during mode switching from SOEC mode to SOFC mode in the adiabatic environment was explored. The results and the discussions focus on the SOC stack only, i.e. not taking into account the BOP components and the durability of the SOC stacks. For example, an optimum inlet gas temperature depends on not only the stack transient performance, but also the lifetime and cost of stack components and BOP components, where the latter may play a more important role. Increasing the stack operation pressure reduces stack temperature variation and hence increases the reversible efficiency of the SOC stacks, but also adds complexity into the reversible system and may not necessarily increase the system efficiency. Further work is needed to extend our current study to the system level, which is ongoing and the results will be presented in our future work.

5 Conclusions

A dynamic model of the SOC stack based on the lumped parameter method was developed and validated with experimental data. Based on this model, the effects of representative factors on the SOC transient performance during mode switching processes in an adiabatic environment were explored via an extensive parametric study. The main conclusions of this study are as follows.

- 1) With the increasing of x_{H_2} from 0.2 to 0.6 (while keeping other parameters constant), the temperature fluctuation range (ΔT_s) and the temperature variation rate ($\left| \frac{dT_s}{d\tau} \right|$) decrease by 25%. V_s increases by 10%, and the increase in η_{re} is 2.91%.
- 2) The inlet work medium temperature (T_{in}) affects the thermal status of the stack during the transient processes. With T_{in} increasing from 973 K to 1273 K, ΔT_s decreases to some extent, but the maximum value of $\left| \frac{dT_s}{d\tau} \right|$ decreases by approximately 30%. In the SOEC mode, the peak voltage of V_s decreases from 9.9 V to 7.8 V, whereas in SOFC mode, the minimum value of V_s increases from 6.5 V to 7.0 V. η_{re} increases by 13.13%.
- 3) With dimensionless stack pressure (R_p) increasing from 1.0 to 4.0, ΔT_s decreases from 32 K to 24 K, $\left| \frac{dT_s}{d\tau} \right|$ decreases by 25%, V_s increases by 0.5%, and η_{re} increases by 1.8%.
- 4) With the dimensionless current density (R_I) increasing from 0.5 to 3.0, ΔT_s increases from 15 K to 120 K, and the maximum value of $\left| \frac{dT_s}{d\tau} \right|$ increases by nearly 10 times. The variation range of V_s also increases significantly. η_{re} decreases by 25.3%.
- 5) With the dimensionless mode switching frequency (R_f) increasing from 1.0 to 4.0, the variation range of T_s decreases from 15 K to 5 K. The variation range of $\left| \frac{dT_s}{d\tau} \right|$ remains almost unchanged. The maximum value of V_s decreases by 1.7% (SOEC), the minimum value increases by 2.0% (SOFC), η_{re} increases with R_f and the maximum difference is 3.16%.
- 6) With the dimensionless heat capacity of the stack (R_{Cs}) increasing from 1.0 to 4.0, ΔT_s decreases from 32 K to 8 K, and $\left| \frac{dT_s}{d\tau} \right|$ decreases accordingly. V_s is almost unaffected, and η_{re} increases from 89.92% to 90.39%.

In summary, to reduce stack-temperature variation and hence extend the stack operational life, larger heat capacity of the stack and higher hydrogen molar fraction (x_{H_2}) of fuel electrode feed gases are proposed. From a stack point of view, higher operation pressure and lower current density are beneficial for increasing the reversible efficiency.

Nomenclature

Abbreviations

<i>ASR</i>	area specific resistance
<i>BOP</i>	balance of plant
<i>SOC</i>	solid-oxide cells
<i>SOEC</i>	solid-oxide electrolysis cell
<i>SOFC</i>	solid-oxide fuel cell
<i>SRU</i>	single repeating unit
<i>TPB</i>	three phases boundary

Greek symbols

τ	time
η	efficiency

Subscript

<i>Cs</i>	heat capacity of the stack
<i>f</i>	furnace
<i>f</i>	switching frequency
<i>I</i>	current density
<i>in</i>	inlet value
<i>out</i>	outlet value
<i>p</i>	pressure
<i>re</i>	reversible efficiency
<i>s</i>	stack
<i>0</i>	initial value

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