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DYNAMIC CHARACTERISTICS OF A SOLID OXIDE CELL STACK UNDERGOING MODE STEP-SWITCHING OPERATION IN AN ADIABATIC ENVIRONMENT

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ABSTRACT

Solid oxide cell stacks can be operated in fuel cell and electrolysis modes according to the electricity demand. Dynamic characteristics of the stack in an adiabatic environment undergoing mode step-switching was presented and analyzed in this paper. Stack temperature and its variation rate, and stack voltage and power output are illustrated. The round trip efficiency (η) of the stack during a switching transient process was calculated and compared when adopting different operational turns. For switching modes, round trip efficiencies of two different processes are 87.4% and 84.6%, respectively.

Keywords: reversible solid oxide cells, dynamic model, clear energy storage, hydrogen power generation.

NONMENCLATURE

Abbreviations	
A	Area
C	Heat capacity of the stack
E	Nernst potential voltage/Energy
F	Faraday constant
j	Current density
h	Enthalpy of the work gases
M	Molarity of gas or stack mass
N	Number of the cell in the stack
P	Pressure
Q/q	Heat
R	Resistance
S	Entropy
SOC	Solid Oxide Cell
SOFC	Solid Oxide Fuel Cell
SOEC	Solid Oxide Electrolysis Cell
T	Temperature
V	Voltage
W	Power supply
τ	Time
σ	Boltzmann constant
Symbols	
act	Activity overpotential
Diffu	Diffusion overpotential
ext	External
react	Chemical reaction
in	Input electricity power
Int	Internal
F	Furnace
ohm	Ohm overpotential
out	Output electricity power
s	Stack
r	Restrict

1. INTRODUCTION

The increasing penetration ratio of renewable power in the power grid necessitates energy storage and conversion technology. Solid oxide cell stack can work in both fuel cell (SOFC) mode to generate power and electrolysis cell (SOEC) mode to convert power to chemical energy stored in gases [1]. Reversible solid oxide cells (SOC) attract the researchers' attention due to their high energy conversion efficiency and operational flexibility. Many researchers focus their attentions on developing models of SOC from 0 to 3D [2-5]. However, most of their studies are on the operational performances of SOC in furnace environment. While in a real operational SOC power generation plant, SOC works

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in a nearly adiabatic environment. The thermodynamic performances of SOC during transient processes affect the SOC electricity power output, and vice versa.

In this work, a dynamic model of SOC coupled with thermodynamics and electrochemistry was developed and validated against experimental data. The exploration of dynamic behaviors of the SOC stack by step switching mode process in an adiabatic environment was then be carried out.

2. DYNAMIC MODELS OF AN SOC STACK

2.1 Two operation modes of a SOC stack

Solid oxide cell stack can work in fuel cell (SOFC) and electrolysis cell (SOEC) modes by controlling the current directions. In SOFC mode, H_2 losses electrons to produce H^+ in anode electrode. Meanwhile, O_2 obtains electrons to produce O^{2-} in cathode electrode. O^{2-} can be conducted through the electrolyte. The mobility of the electrons can produce electricity to supply to the external load. In SOEC mode, the reactions are inversed totally. Electricity is needed to drive the electrochemical reactions to produce H_2 and O_2.

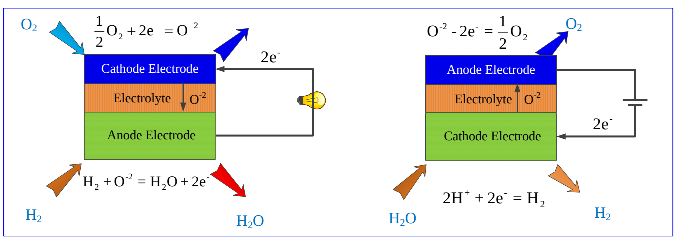


Fig 1 Two operation modes of SOC

Three main electrochemical reactions occur in SOC:

$$H_2 - 2e^- \leftrightarrow 2H^+$$

$$\frac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-}$$

$$2H^+ + O^{2-} \leftrightarrow H_2O$$

In SOFC mode, the reactions occure from left to right side, and the total reaction is exothermic. In SOEC mode, the recitons occur from right to left side, and the total reaction is endothermic.

2.2 Model development, calibration and validation

For developing the dynamic model briefly, following assumptions were made:

(a)The work fluids are homogeneous and continuous; (b) The lump parameter method is adopted for the solid oxide cell stack; (c) Ideal gas properties are adopted for all the work gases; (d) The thermal inertial of the storage work medium in the stack is neglected. And the detailed dynamic model is shown in Table 1.

Table 1. Summary of the coupled dynamic models

Governing equation
Thermodynamic models
Mass and momentum conservation in bulk ($\emptyset$ is -1 and +1 for consumption and production)
$(dM_i)/d\tau = \dot{m}_{\mathrm{in,i}} - \dot{m}_{\mathrm{out,i}} + \emptyset \cdot \dot{m}_{\mathrm{react,i}}$ $R_r \cdot \dot{m}_{\mathrm{total}}^2 = P_{\mathrm{in}} - P_{\mathrm{out}}$ $\dot{m}_{\mathrm{total}} = \sum \dot{m}_{\mathrm{out,i}}$
Energy conservation in bulk $C_s\, dT_s/d\tau = \sum \dot{m}h - \dot{W} + \dot{Q}_{\mathrm{react}} + \dot{Q}_{\mathrm{ext}} + \dot{Q}_{\mathrm{int}}$ $\dot{W} = N\ V_{\mathrm{cell}}\ j\ A_{\mathrm{cell}}$ $\dot{Q}_{\mathrm{react}} = jNA_{\mathrm{cell}}/2F\ \dot{q}_{\mathrm{react}}$ $\dot{Q}_{\mathrm{ext}} = \sigma \cdot (T_f^4 - T_s^4) \cdot A_{\mathrm{sur}}$ $\dot{Q}_{\mathrm{int}} = j(V_{\mathrm{act}} + V_{\mathrm{ohm}})A_{\mathrm{cell}} - jA_{\mathrm{cell}}T_s\Delta S^0/2F$ $\Delta S^0 = \Delta S^0_{\mathrm{H_2O}} - (\Delta S^0_{\mathrm{H_2}} + 0.5 \cdot \Delta S^0_{\mathrm{O_2}})$
Electrochemical model
$V_{\mathrm{cell}} = E_{\mathrm{nernst}} - V_{\mathrm{act}} - V_{\mathrm{ohm}} - V_{\mathrm{diffu}}$ $V_s = N\ V_{\mathrm{cell}}$

Switching mode between SOFC and SOEC in ramp format with current density varying from -0.25 to 0.25 A cm^{-2} is adopted to test the dynamic model's validity. The process is simulated and validated with experimental data obtained on an 8-cell experimental stack tested at the Technical University of Denmark [[6]]. The input variable is the current density (I), and the key output parameters are the stack voltage (V_s), stack power output (W) and stack temperature (T_s). The variation in I, V_s, W and T_s are illustrated in Fig.2 (a) to (d), respectively. As the observations in Fig.2 (b) to (d), the maximum deviation in V_s and T_s are 0.3 V and 8K, which account for 4% and 0.1%. The deviation of W is not obvious. The comparison of the simulated and experimented results validate the accuracy of the stack dynamic models.

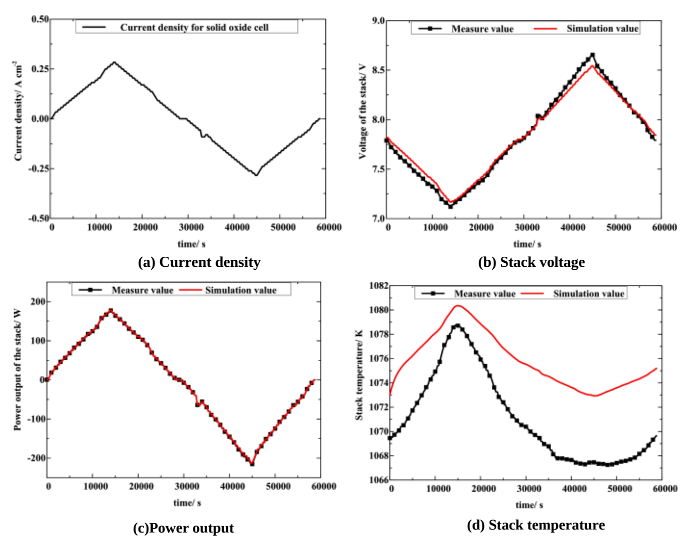


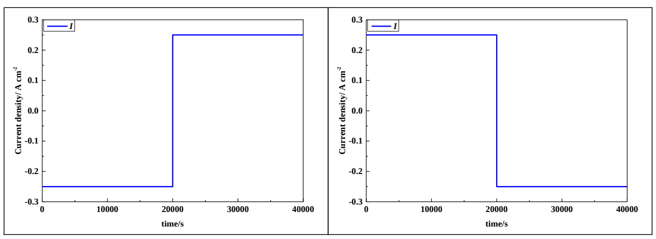
Fig 2 Key parameters' trend profile during transients

3. RESULTS AND DISCUSSIONS

In the real operational solid oxide cell stack power generation stations, the furnace may not be supplied to stabilize the stack temperature. The stack works in an adiabatic space, nearly. In most cases, the SOC system works with reversible source power generation station, such as wind power generation or solar power station. The unpredicted weather affects the real time output. The SOC system may switch mode frequently to mitigate the power output fluctuation. Step switching mode is the most typical format.

3.1 Step switching mode

Fig 3 (a) and (b) shows the current density variation for switching modes between SOFC and SOEC. The variation range of current density is -0.25 to 0.25A cm^{-2}.



(a) SOEC to SOFC (B) SOFC to SOEC

Fig 3 Switching mode between SOFC and SOEC

The detailed parameters of the stack and the boundary conditions are shown in Table 2 and 3.

Table 2. Detailed parameters of the stack

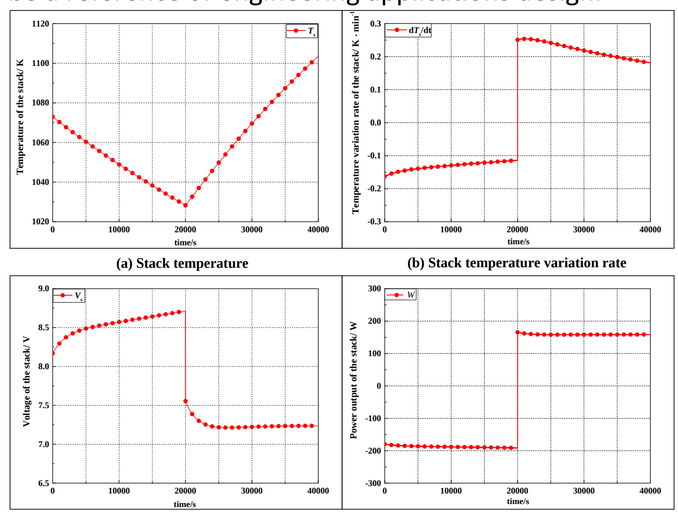
Parameter	Unit	Value
c_s	J kg^{-1} K^{-1}	5.00×10^{2}
M_s	kg	3.70×10^{1}
N		8.00×10^{0}
A_{cell}	m^{2}	8.77×10^{-3}
A_{sur}	m^{2}	7.00×10^{-2}
σ	W·m^{-2}·K^{-4}	5.67×10^{-8}
R_r	kg^{-2} MPa s^{2}	1.00×10^{0}

Table 3. Input boundaries of the experimental stack

Term	Gas	Flowrate/ sccm cm^{-2}	Temperature/K
Anode	H_2	6.22	1033
	H_2O	6.22	1033
Cathode	O_2	5.70	1033

3.2 Dynamic response of the stack

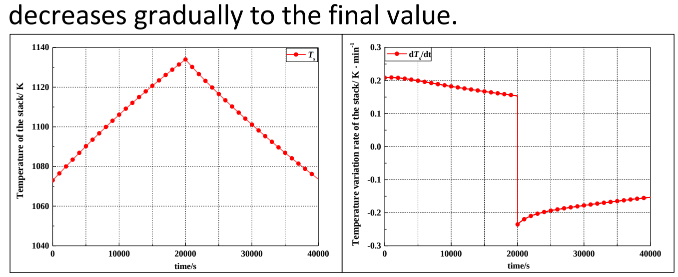
For the stack mode switching from SOEC to SOFC process, in the beginning of the operation, the current density (I) is zero. When time is 0, I increases from 0 to -0.25A cm^{-2} suddenly. When time is 20000s, I jumps to +0.25A cm^{-2}. Fig.4 illustrates variation of key parameters during transients. In SOEC mode, endothermal reactions occur and stack temperature (T_s) decreases from 1073 to 1025K. The variation rate of T_s ($\frac{dT_s}{d\tau}$) is negative, which varies from -0.16 to 0.12 K min^{-1}. The voltage of the stack (V_s) gradually increases from 8.2 to 8.7 V. The power output (W) is negative. After switching mode from SOEC to SOFC, T_s increases from 1025 to 1103K in 20000s. ($\frac{dT_s}{d\tau}$) varies from -0.12 to 2.2 K min^{-1}. ($\frac{dT_s}{d\tau}$) decreases to 0.18 gradually. V_s decreases from 8.7 to 7.6V directly, and gradually decreases to 7.2V. W varies from a negative value to a positive one. After the sudden variation, W reaches to the peak value and gradually decreases to a stable value. The stack temperature variation range can be a reference of engineering applications design.



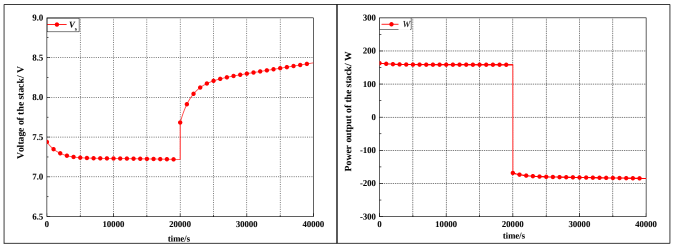
(a) Stack temperature (b) Stack temperature variation rate
(c) Stack voltage (d) Stack power output

Fig 4 Dynamic response of the stack during SOEC to SOFC

Fig.s 5 (a) to (d) show the curves of T_s, ($\frac{dT_s}{d\tau}$), V_s and W during SOFC to SOEC transients. After I increases from 0.0 to 0.25A cm^{-2} in steps, exothermal reactions occur and T_s increases from 1073 to 1135K until I varies to -0.25A cm^{-2}. ($\frac{dT_s}{d\tau}$) decreases from 0.2 to 0.15K min^{-1}. V_s decreases from 7.5 to 7.25V gradually. W is positive and stable. After the sudden change in I, T_s decreases obviously from 1135 to 1075K. ($\frac{dT_s}{d\tau}$) varies from -0.24 to 0.15K min^{-1}. V_s increases from 7.25 to 7.6V suddenly and afterwards gradually to 8.4V. W is negative and decreases gradually to the final value.



(a) Stack temperature (b) Stack temperature variation rate



(c) Stack voltage (d) Stack power output

Fig 5 Dynamic response of the stack during SOFC to SOEC

3.3 Energy delivery characteristics during transients

For the total processes of switching between SOFC and SOEC transients, electrical energy is converted to chemical energy in SOEC mode and the reverse process occurs in SOFC mode. The round trip efficiency (η) of SOEC-SOFC switching can be calculated by the following expressions:

For SOFC-SOEC switching process:

$$E_{\_\mathrm{In}} = \int_{20000}^{40000} \dot{W}\, d\tau$$

$$E_{\_\mathrm{Out}} = \int_{0}^{20000} \dot{W}\, d\tau$$

$$\eta_{\mathrm{SOFC-SOEC}} = \frac{E_{\_\mathrm{Out}}}{E_{\_\mathrm{In}}}$$

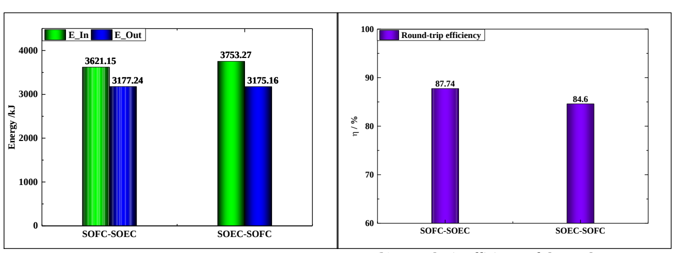
For SOEC-SOFC switching process:

$$E_{\_\mathrm{In}} = \int_{0}^{20000} \dot{W}\, d\tau$$

$$E_{\_\mathrm{Out}} = \int_{20000}^{40000} \dot{W}\, d\tau$$

$$\eta_{\mathrm{SOEC-SOFC}} = \frac{E_{\_\mathrm{Out}}}{E_{\_\mathrm{In}}}$$

Fig.6 (a) shows the input electrical power (SOEC) and output electrical power (SOFC) mode during switching mode processes. Fig.6 (b) illustrates η of the switching mode SOFC-SOEC and SOEC-SOFC processes, respectively. The results show that $\eta_{\mathrm{SOFC\text{-}SOEC}}$ is higher than $\eta_{\mathrm{SOEC\text{-}SOFC}}$. The difference in $\eta_{\mathrm{SOFC\text{-}SOEC}}$ and $\eta_{\mathrm{SOEC\text{-}SOFC}}$ is 3.14%.



(a) Energy input and output (b) Round trip efficiency of the stack

Fig 6 Energy delivery efficiency of the stack during switching between SOEC and SOFC mode

4. CONCLUSIONS

Solid oxide cell (SOC) stacks may operate in transient processes to mitigate the fluctuation of the renewable power. Switching modes between SOEC and SOFC is a typical transient process. In this paper, a dynamic model of SOC stack was developed and validated by experimental data. Based on this model, dynamic responses of the stack undergoing step switching mode format in an adiabatic environment was studied and analyzed in detail. Stack temperature variation trends and ranges, stack voltage and stack power output were presented during switching mode transients. The round-trip efficiency of switching modes between SOFC and SOEC were compared when adopting different turns. The results show that T_s has to undergo a period of increased stack temperature for switching SOFC to SOEC processes and η of SOFC to SOEC is higher than that of SOEC to SOFC. Results can be a reference of engineering design.

ACKNOWLEDGEMENT

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