Thermal effects in H$_2$O and CO$_2$ assisted direct carbon solid oxide fuel cells

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HIGHLIGHTS

- Model for the thermal effect in CO$_2$ and H$_2$O assisted DC-SOFC is developed.
- The heat generation/consumption are both much higher in H$_2$O assisted DC-SOFC.
- A thermal neutral voltage is observed.
- High anode inlet gas flow rate is not necessary.
- A smaller distance between the carbon and the anode is beneficial.

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ABSTRACT

Thermal effects in a H$_2$O and CO$_2$ assisted tubular direct carbon solid oxide fuel cell (DC-SOFC) are numerically investigated. Parametric simulations are further conducted to study the effects of operating potential, the distance between carbon and anode, inlet gas temperature, and anode inlet gas flow rate on the thermal behaviors of the fuel cell. It is found that the fuel cell with H$_2$O as gasification agent performs considerably better than the cell with CO$_2$ as gasification agent in all cases. It is also found that the temperature field of the fuel cell is highly uneven. The breakdown of the heat sources in the fuel cell shows that the H$_2$O assisted DC-SOFC has much higher heat generation and consumption than the CO$_2$ assisted cell. Interestingly, a thermal neutral voltage is observed, at which no heating or cooling of the cell is needed. In addition, the distance between the anode and the carbon layer is required to be as small as possible, which improves the temperature uniformity of the fuel cell. The results of this study demonstrates the importance of thermal effects in DC-SOFCs and form a solid foundation for DC-SOFC thermal management.

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Introduction

The growing concern of the whole human society to environmental problems and energy crisis has promoted the worldwide research on clean and efficient energy technologies [1–3]. Although renewable wind and solar energy will play more and more pivotal role in energy supply, the main energy sources will continue to be fossil fuels in the coming decades [4]. Conventional technologies for power generation from fossil fuels are based on heat engines, which not only cause pollutant emissions including SOx, CO2, and NOx, but also low energy conversion efficiency (30–40%) [5]. Therefore, advanced energy conversion technologies with higher efficiency and lower emission are urgently needed to more efficiently and cleanly convert fossil fuels into electrical power.

As one of the most competitive clean and highly efficient devices to convert fuels to electricity, solid oxide fuel cell (SOFC) has received rising interest [6–10]. A typical SOFC has a sandwiched structure, including a dense electrolyte in the middle for O2− ions transportation and two side porous electrodes for electrochemical reactions. Unlike conventional power plants based on thermodynamic cycles involving combustion process, through electrochemical reactions, the chemical energy of fuels can be converted into power by SOFCs. As the energy conversion process in SOFCs is not a thermodynamic cycle, the Carnot cycle efficiency does not limit the energy efficiency. The energy efficiency of SOFCs can be higher than 50%, which is significantly higher than that of a coal-fired power plant. In addition, the dense electrolyte of SOFCs can separate the emission gases and make the emission control and post treatment easier. Therefore, SOFCs are promising to replace conventional power plants. Compared with other types of fuel cells requiring pure H2 as fuel, such as proton exchange membrane fuel cells (PEMFCs), SOFCs are very fuel flexible as various alternative fuels can be used for power generation, including H2, CO, methane, biogas, ethanol, NH3, and solid carbon.

To achieve a higher energy density and lower overall cost, solid fuels are more attractive than gaseous fuels. The direct carbon solid oxide fuel cells (DC-SOFCs) have been developed in order to utilize the solid carbon in SOFCs directly. As solid carbon particles are much bigger than the pore size of the porous anode, the carbon fuel cannot enter the porous anode layer to be electrochemically oxidized. The solid carbon fuel needs to be gasified by H2O or CO2 to form gaseous fuels (e.g. CO and H2), which are electrochemically oxidized for power generation. At the cathode side, air is supplied to the cathode chamber. O2 molecules are conveyed through the porous cathode to the triple phase boundary (TPB) and are reduced (combined with electrons) to oxygen ions (O2−). The produced oxygen ions (O2−) are conveyed through the dense electrolyte to the anode side for oxidizing the gaseous fuels (e.g. CO and H2) and producing electrons.

Most of DC-SOFCs employ CO2 for carbon gasification (C + CO2 = 2CO), which is termed as reversible Boudouard reaction. Nakagawa et al. [11] firstly tested high-temperature DC-SOFC with CO fuel from gasification of charcoal. They proposed that the CO was electrochemically oxidized at the anode of DC-SOFC. Liu et al. [12] developed a novel tubular DC-SOFC which firstly used carbon black as fuel. In their preliminary examination, the DC-SOFC delivered a maximum power density of 104 mW cm−2 at 1123 K. A DC-SOFC 3-cell-stack by Bai et al. [13] achieved a peak power output of 2.4 W and a volumetric power density of 700 mW cm−3 at 1123 K. All these experimental results demonstrate the feasibility of DC-SOFCs for power generation from carbon. However, the DC-SOFCs need to be operated at a high temperature (i.e. 1123 K) due to the slow reversible Boudouard reaction for carbon gasification by CO2. In order to enhance the Boudouard reaction to facilitate CO generation from carbon, various catalysts have been developed for the Boudouard reaction. Wu et al. [14] enhanced carbon gasification reaction rate by adopting...
Fe₉O₈-MₙO (M = Li, K, Ca) for catalyzing the Boudouard reaction in the DC-SOFC and attained a maximum power density of 297 mW cm⁻² at 1123 K, which was only slightly lower than that achieved using gaseous H₂ as fuel. In a study conducted by Jiao et al. [15], they used alkali to treat the coal char and found its specific surface area was enlarged so that the Boudouard reaction rate and the power output were consequently improved. The peak power density reached 220 mW cm⁻² at 1123 K for modified coal char, which was much higher than 62 mW cm⁻² for conventional coal char. Wu et al. [16] developed DC-SOFC using brown coal with abundant Ca element as fuel to achieve a maximum power density of 221 mW cm⁻² at 1123 K. M. Dudek et al. [17] used the direct ceramic inkjet printing technology to make cermetallic multicomponent anode material for DC-SOFC. The Cu modified Ni YSZ anode showed a secondary catalytic effect of CO generation in the Boudouard reaction. Wang et al. [18] fabricated a DC-SOFC stack with 4-cells-in-series on a single yttrium-stabilized-zirconia electrolyte plate, which could deliver 8.6 W h at 1093 K, discharging at 200 mA for 14 h. The above-mentioned studies on DC-SOFC with CO₂ as carbon gasification demonstrated the feasibility of this technology and the importance of the carbon gasification process. Although the use of catalyst for the Boudouard reaction can enhance the carbon gasification kinetics to some extent, it is still insufficient. As a result, the operating temperature can hardly be lowered than 1123 K, which is too high for efficient and durable operation of DC-SOFC.

Some researchers tried to improve the efficiency of DC-SOFC through other ways. Guo et al. [19] employed dual chamber with all porous electrolyte structure to develop the DC-SOFC. They successfully controlled the needed oxygen at the anode side, which avoided coke formation on the anode side. Wu et al. [20] developed a high performance DC-SOFC. The cell can achieve power densities of 188, 108 and 48 mW cm⁻² at 873, 823, and 773 K, respectively. In their experiments, Zhou et al. [21] found that CO–CO₂ counter diffusion affected the DC-SOFC performance significantly, which was closely related to the distance between carbon and anode. This counter diffusion was more important at lower temperature and higher current. Wang et al. [22] studied the effects of fuel treating temperature and discharge mode on the fuel utilization of DC-SOFC and found that higher fuel utilization can be achieved by higher coal temperature and constant resistance mode.

In recent years, it is found that the operating temperature of DC-SOFC can be lowered without sacrificing the performance by using H₂O to replace CO₂ for carbon gasification. Thermodynamic analyses conducted by Lee et al. [23] indicate little variation in the DC-SOFC efficiency or work output between the CO₂ and H₂O as gasification agents. However, their thermodynamic analyses totally neglected the effects of H₂O and CO₂ on the carbon gasification kinetics, thus their study could not truly reflect the effects of gasification agents on the performance of DC-SOFC. Ong and Ghoniem [24] developed a 1D membrane-electrode-assembly model to study the

Fig. 1 – Schematic of CO₂ assisted DC-SOFC (a) and H₂O assisted DC-SOFC (b).
indirect-carbon solid oxide fuel cell (IC-SOFC) with carbon gasification by H₂O or CO₂ in an external gasifier. It was evident from the numerical study that between 973 K and 1023 K the IC-SOFC performed 3–5 times better with H₂O than CO₂ recycling. This modeling study provided a good foundation to clarify the difference between CO₂ dry gasification and H₂O assisted DC-SOFC (H₂O case). The 2D mathematical model is developed to simulate the heat transfer, ion/electron transport, mass/momentum transport and chemical/electrochemical reactions in the DC-SOFC. The anode chamber is filled with porous solid carbon, which is placed very close to the porous anode. The CO₂ or H₂O is supplied as the gasification agent at the inlet of the anode chamber to react with the solid carbon inside the whole anode chamber. The original model details have been reported in our previous work [25], which has been well validated. The assumptions made in Ref. [25] are adopted in the present investigation. In the porous electrode, TPBs are distributed uniformly and the electronic/ionic conducting phases are continuous and homogeneous. All gases are assumed as ideal gases, and gas flow is laminar and incompressible.

Compared with the previous work, the geometry model is extended from button cell to tubular cell for practical application consideration. The electrochemical part of the cell has a length of 10 mm, an inner diameter of 12 mm and an outer diameter of 12.864 mm. The modeled tubular cell uses Ni-YSZ (yttrium stabilized zirconium) composites as anode, bilayer YSZ/samarium-doped CeO₂ (SDC) electrolyte and LSCF (lanthanum strontium cobalt ferrite) as cathode. The thickness of the anode, electrolyte and cathode are 400 μm, 8 μm and 24 μm, respectively. The distance between carbon and anode is 550 μm. Over a certain operation period, the amount of carbon in the carbon chamber can be assumed to be constant. Thus the DC-SOFC is assumed to be under steady state operating conditions. Tables 1–2 list the material properties, including the ionic/electronic conductivity, porosity, anode volume fraction, TPB active area per unit volume (S_TPB), the thermal conductivity λ, specific heat capacity c, and density ρ, respectively. The thermal radiation is assumed to be negligible.

The reaction model

Chemical reactions

For the traditional DC-SOFC, the Boudouard reaction (C+CO₂ ↔ 2CO) plays a major role because it produces CO for the reaction model.

**Computational setup**

*Description of computational model*

Fig. 1 presents a schematic diagram of the CO₂ assisted DC-SOFC (CO₂ case) and H₂O assisted DC-SOFC (H₂O case). The reaction model is coupled with electrochemical reactions in the DC-SOFC. The carbon gasification reaction kinetics and the electrochemical oxidation in the anode, the maximum power density was improved from 158 mW cm⁻² in CO₂ case to 385 mW cm⁻² in H₂O case at 1123 K. Moreover, the in situ steam carbon gasification reaction was observed significantly speeding up by adding Na₂CO₃ as catalyst, which can improve the performance of H₂O assisted DC-SOFC. However, the temperature field of DC-SOFC was assumed uniform and the thermal effect was not taken into consideration in these studies.

The complex gas transport, heat transfer and the electrochemical/chemical reactions are all highly coupled in DC-SOFC. The carbon gasification reaction kinetics and the electrochemical processes are all temperature-dependent. The temperature field/thermal effect have significant impact on the performance of DC-SOFC. In order to fill the research gap, the model developed in previous study [25] is extended to investigate the thermal effects on the temperature distribution of DC-SOFC with both CO₂ and H₂O as carbon gasification agent.

**Table 1** – Material electric properties [27–31].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Expression or Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic conductivity</td>
<td>3.4×10⁶</td>
<td>4200</td>
</tr>
<tr>
<td>YSZ</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>SDC</td>
<td>4.25</td>
<td>4.25</td>
</tr>
<tr>
<td>LSCF</td>
<td>4.25</td>
<td>4.25</td>
</tr>
<tr>
<td>Electronic conductivity</td>
<td>3.4×10⁶</td>
<td>100</td>
</tr>
<tr>
<td>Ni</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>LSCF</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.6</td>
<td>/</td>
</tr>
<tr>
<td>Anode</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Cathode</td>
<td>0.2</td>
<td>/</td>
</tr>
<tr>
<td>Anode volume fraction</td>
<td>0.6</td>
<td>/</td>
</tr>
<tr>
<td>Ni</td>
<td>0.6</td>
<td>/</td>
</tr>
<tr>
<td>YSZ</td>
<td>0.4</td>
<td>/</td>
</tr>
<tr>
<td>S_TPB</td>
<td>3</td>
<td>/</td>
</tr>
<tr>
<td>Electrode tortuosity</td>
<td>2.14×10⁶</td>
<td>m² m⁻³</td>
</tr>
<tr>
<td>Anode layer</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Cathode layer</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

**Table 2** – Material thermodynamic properties [32–38].

<table>
<thead>
<tr>
<th>Materials</th>
<th>λ (W m⁻¹ K⁻¹)</th>
<th>c (J kg⁻¹ K⁻¹)</th>
<th>ρ (kg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>1.59</td>
<td>887.5</td>
<td>1700</td>
</tr>
<tr>
<td>Ni-YSZ</td>
<td>6.23</td>
<td>390.0</td>
<td>6870</td>
</tr>
<tr>
<td>SDC</td>
<td>1.77</td>
<td>450.0</td>
<td>7120</td>
</tr>
<tr>
<td>YSZ</td>
<td>2.57</td>
<td>525.0</td>
<td>6086</td>
</tr>
<tr>
<td>LSCF</td>
<td>2.00</td>
<td>568.0</td>
<td>6360</td>
</tr>
</tbody>
</table>

**Table 3** – Chemical reaction parameters.

<table>
<thead>
<tr>
<th>Parameters (Unit)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₁ (s mol kg⁻¹ m⁻³)</td>
<td>9.32×10⁻⁴</td>
</tr>
<tr>
<td>K₂ (Pa⁻¹)</td>
<td>1.25×10⁻⁵</td>
</tr>
<tr>
<td>K₃ (Pa⁻¹)</td>
<td>3.82×10⁻⁵</td>
</tr>
<tr>
<td>K₄ (s mol kg⁻¹ m⁻³)</td>
<td>2.19×10⁻⁵</td>
</tr>
<tr>
<td>K₅ (Pa⁻¹)</td>
<td>9.88×10⁻⁶</td>
</tr>
<tr>
<td>K₆ (Pa⁻¹)</td>
<td>8.13×10⁻⁷</td>
</tr>
</tbody>
</table>
subsequent electrochemical reaction, where solid carbon is
the energy source and CO acts as an energy carrier to trans-
port chemical energy from solid carbon to anode TPB. By
adding H₂O to DC-SOFC, the H₂O gasification reaction
\((C + H₂O → CO + H₂)\) replaces the Boudouard reaction and be-
comes the main chemical-reaction in the anode chamber as

\[
\begin{align*}
\gamma_{eCO} (\text{A m}^{-2}) & = 2.944 \times 10^{10} \\
E_{\text{act,H}_2} (\text{J mol}^{-1}) & = 1.2 \times 10^5 \\
\gamma_{eO_2} (\text{A m}^{-2}) & = 1.390 \times 10^5 \\
E_{\text{act,O}_2} (\text{J mol}^{-1}) & = 1.2 \times 10^5 \\
\gamma_{eCO} (\text{A m}^{-2}) & = 1.673 \times 10^5 \\
E_{\text{act,CO}} (\text{J mol}^{-1}) & = 1.2 \times 10^5 
\end{align*}
\]

H₂O gasification has a much higher reaction rate. The reaction
rate of the Boudouard reaction and H₂O gasification reaction
\([39]\) are expressed in Eqs. (1) and (2).

\[
\begin{align*}
\frac{r_{eCO}}{1 + K_p P_m + K_n P_n} \\
\frac{r_{eH_2O}}{1 + K_p P_m + K_n P_n}
\end{align*}
\]

The widely used chemical reaction parameters are adopted
and listed in Table 3.

<table>
<thead>
<tr>
<th>Table 4 – Electrochemical reaction parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters (Unit)</td>
</tr>
<tr>
<td>(\gamma_{eCO} (\text{A m}^{-2}))</td>
</tr>
<tr>
<td>(E_{\text{act,H}_2} (\text{J mol}^{-1}))</td>
</tr>
<tr>
<td>(\gamma_{eO_2} (\text{A m}^{-2}))</td>
</tr>
<tr>
<td>(E_{\text{act,O}_2} (\text{J mol}^{-1}))</td>
</tr>
<tr>
<td>(\gamma_{eCO} (\text{A m}^{-2}))</td>
</tr>
<tr>
<td>(E_{\text{act,CO}} (\text{J mol}^{-1}))</td>
</tr>
</tbody>
</table>

Fig. 2 – Mesh independence (a) and model validation (b,c).

Fig. 3 – The voltage-current density-power density (a) and
voltage-average cell temperature (b) relationships for CO₂
case and H₂O case.

Table 5 – Operation parameters for operating potential
effect study in DC-SOFCs.

<table>
<thead>
<tr>
<th>Parameters (Unit)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating potential (V)</td>
<td>0–0.8</td>
</tr>
<tr>
<td>Anode inlet gas flow rate (SCCM)</td>
<td>10</td>
</tr>
<tr>
<td>Cathode inlet gas flow rate (SCCM)</td>
<td>400</td>
</tr>
<tr>
<td>Anode gas composition for H₂O/CO₂ assisted DC-SOFC</td>
<td>100%</td>
</tr>
<tr>
<td>Cathode gas composition</td>
<td>Air</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>1123</td>
</tr>
</tbody>
</table>
The nickel-catalyzed water gas shift reaction (WGSR) (CO + H₂O ↔ CO₂ + H₂) in the anode electrode is also an important chemical reaction and is fully considered in the model. This reaction converts CO into H₂ and ensures H₂ to mainly participate in electrochemical reaction. The reaction rate of WGSR [40] is expressed in Eqn. (3).

\[
\dot{r}_{\text{WGSR}} = a \left( \frac{P_{\text{H}_2}\text{O}P_{\text{CO}} - P_{\text{H}_2}P_{\text{O}_2}}{b} \right)
\]

where
\[
a = 0.0171e^{-\frac{8188}{RT}} (\text{mol m}^{-3}\text{Pa}^{-2}\text{s}^{-1})
\]
\[
b = e^{-\left(0.29352^2 + 0.6352^2 + 4.17882 + 0.3169\right)} \approx 1000
\]

In summary, the water gasification reaction replaces the Boudard reaction and becomes the main chemical reaction for H₂O case. It should be noted that the electrochemical oxidation of H₂ is much easier than that of CO in SOFC. By introducing H₂O into DC-SOFCs, better electrochemical reaction activity can be achieved due to more rapid gas fuel production rate.

Electrochemical reactions
For the CO₂ case, the CO is the only fuel that is electrochemically oxidized in the DC-SOFC anode. While for the H₂O case, both CO and H₂ will be produced in the chemical reactions and participate in the electrochemical reactions: CO + O²⁻ → CO₂ + 2e⁻, and H₂ + O²⁻ → H₂O + 2e⁻.

The operating potential \( V \) is expressed in terms of the thermodynamic equilibrium potential \( E_{\text{eq}} \) and operating activation/ohmic overpotential losses in Eqn. (4).

\[
V = E_{\text{eq}} - \eta_{\text{ohmic}} - \eta_{\text{act}}
\]

where \( \eta_{\text{ohmic}} \) and \( \eta_{\text{act}} \) are the ohmic overpotential and activation overpotentials, respectively. The \( \eta_{\text{ohmic}} \) is related to the ionic/electronic conductivity and current intensity of the cell. More detailed information can be found in our previous work [41–43]. The potential obstacle for the electrochemical reaction is expressed as the activation overpotential \( \eta_{\text{act}} \). The relationship between the \( \eta_{\text{act}} \) and the current density can be described by the Butler-Volmer equation as shown in Eqn. (5).

\[
i = i_0 \left( e^{\frac{\eta_{\text{act}}}{\gamma}} - e^{-\frac{\eta_{\text{act}}}{\gamma}} \right)
\]

where the \( \gamma \) and \( E_{\text{act}} \) are the pre-exponential factor and the activation energy level, respectively. In the present study, the typical values of \( \gamma \) and \( E_{\text{act}} \) are adopted and listed in Table 4.

The \( E_{\text{eq}} \) is determined by the thermodynamic properties of the reaction: reaction enthalpy, entropy, and Gibbs free energy. For the CO₂ case, the equilibrium potential can be calculated by the Nernst equation, since only CO participate in the electrochemical reaction, as shown in Eqn. (7). However, both CO and H₂ can take part in the electrochemical reaction for the H₂O case. The \( E_{\text{eq}} \) for CO/H₂ fuels can be determined by Eqsns. (7) and (8) respectively in this situation. Noted that the \( E_{\text{eq}} \) calculated by Eqsns. (7) and (8) are equal under an open-circuit condition. The \( E_{\text{eq}} \) for CO and H₂ fuels become different, when current is extracted from the DC-SOFC, due to the different overpotential losses involved in electrochemical oxidation of the CO/H₂ fuel.

\[
E_{\text{CO}} = E_{\text{CO}}^0 + \frac{RT}{2F} \ln \left[ \frac{P_{\text{CO}}}{P_{\text{CO}_2}} \right]^{0.5}
\]

\[
E_{\text{H}_2} = E_{\text{H}_2}^0 + \frac{RT}{2F} \ln \left[ \frac{P_{\text{H}_2}}{P_{\text{H}_2}O} \right]^{0.5}
\]
where the $E^0$ and $P$ are the standard potential and the local gas partial pressure, respectively. Then the values of the standard potential of carbon monoxide oxidation and hydrogen are expressed in Eqn. (9).

\[
\begin{align*}
E_{\text{CO}}^0 &= 1.46713 - 0.00045270T \\
E_{\text{H}_2}^0 &= 1.25300 - 0.00024516T
\end{align*}
\]

Heat and mass transfer model

For the fluid flow, the classic Navier-Stokes equation with the Darcy’s term is adopted to describe the momentum transport of gas species in both the gas channel and the porous electrodes as shown in Eqn. (10)

\[
\frac{\partial u}{\partial t} + \mu u \nabla u = -\nabla p + \mu \left[ (\nabla u + (\nabla u)^T) - \frac{2}{3} \mu \nabla \right] - \frac{\epsilon \mu u}{k}
\]

When the last term on the right side of Eqn. (10) is removed, the equation is simplified to the traditional N–S equation for momentum conservation of gas flows. $k$ is the permeability of the porous electrodes. $\epsilon$ is the porosity of the porous electrodes.

For the mass transport, the rate $N_i$ in channels and the porous electrodes can be expressed by the general Fick’s model [44] as:

\[
N_i = \frac{1}{RT} \left( D_{ij}^m \left( \frac{\partial y_i}{\partial z} - \frac{B_i y_i P}{\mu} \frac{\partial P}{\partial z} \right) \right)
\]

Fig. 5 – Cell temperature distribution with CO$_2$ (a) and H$_2$O (c) as agents and cathode O$_2$ molar fraction with CO$_2$ (b) and H$_2$O (d) as agents at 0.5 V (left) and 0.1 V (right).
where the $B_0$ and $y_i$ are the permeability coefficient of the porous electrodes and the mole fraction of component $i$ $(i = 1, 2, ..., n)$, respectively. The effective diffusion coefficient of component $i$ is expressed as $D_i^{\text{eff}}$ and can be further expressed as Eqn. (12) [45] for gas diffusion in the porous electrodes.

$$D_i^{\text{eff}} = \frac{\varepsilon}{\tau} \left( \frac{1}{D_k^{i}} + \frac{1}{D_m^{i}} \right)^{-1}$$

where $\tau$ is the tortuosity factor. The $D_k^{i}$ and $D_m^{i}$ represent the effective Knudsen diffusion coefficient and the effective molecular diffusion coefficient. The detailed information on diffusion coefficient of $D_k^{i}$ and $D_m^{i}$ can be found in Ref. [46].

Besides, for the heat transfer model, the electrochemical reactions in TPB sites generates heat while the carbon gasification in the anode chamber is highly endothermic. It not only results in the temperature gradient along the cell length, but also along the radial direction. Thus the general heat balance equation is applied to simulate the heat transfer process as Eqn. (13).

$$\rho C_p u \cdot \nabla T + \nabla \cdot (-\lambda^{\text{eff}} \nabla T) = Q$$

where the $C_p$ and $\lambda^{\text{eff}}$ are the fluid thermal capacity and the thermal conductivity, respectively. In this equation, the $\lambda^{\text{eff}}$ depends on the heat conductivity of liquid and solid phase, $\lambda_{s}$ and $\lambda_l$, as the form of $\lambda^{\text{eff}} = (1-\varepsilon) \lambda_s + \varepsilon \lambda_l$ in the porous structure of electrodes. The $Q$ is the heat source term, which represents the heat generation or consumption due to various overpotential losses and chemical/electrochemical reactions. In this paper, the heat source term contains heat consumption of

![Fig. 6](image)

**Fig. 6** – Effects of applied voltage on the heat compositions including CO electrochemical reaction (CER), H$_2$ electrochemical reaction (HER), ohmic overpotential (OO), activation overpotential (AO) and carbon gasification (CG) and net heat (NH) with CO$_2$ (a) and H$_2$O (c) as agents and percentages of different heat sources with CO$_2$ (b) and H$_2$O (d) as agents.

**Table 6** – Operation parameters for anode inlet gas flow rate effect study in DC-SOFCs.

<table>
<thead>
<tr>
<th>Parameters (Unit)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating potential (V)</td>
<td>0.5</td>
</tr>
<tr>
<td>Anode inlet gas flow rate (SCCM)</td>
<td>1–50</td>
</tr>
<tr>
<td>Cathode inlet gas flow rate (SCCM)</td>
<td>400</td>
</tr>
<tr>
<td>Anode gas composition for H$_2$O/CO$_2$ assisted DC-SOFC</td>
<td>100%</td>
</tr>
<tr>
<td>Cathode gas composition</td>
<td>Air</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>1123</td>
</tr>
</tbody>
</table>

- $C_0$ and $y_i$ are the permeability coefficient of the porous electrodes and the mole fraction of component $i$ $(i = 1, 2, ..., n)$, respectively. The effective diffusion coefficient of component $i$ is expressed as $D_i^{\text{eff}}$ and can be further expressed as Eqn. (12) [45] for gas diffusion in the porous electrodes.

- $D_i^{\text{eff}} = \frac{\varepsilon}{\tau} \left( \frac{1}{D_k^{i}} + \frac{1}{D_m^{i}} \right)^{-1}$

The detailed information on diffusion coefficient of $D_k^{i}$ and $D_m^{i}$ can be found in Ref. [46].

- For the heat transfer model, the electrochemical reactions in TPB sites generate heat while the carbon gasification in the anode chamber is highly endothermic. It not only results in the temperature gradient along the cell length, but also along the radial direction. Thus the general heat balance equation is applied to simulate the heat transfer process as Eqn. (13).

$$\rho C_p u \cdot \nabla T + \nabla \cdot (-\lambda^{\text{eff}} \nabla T) = Q$$

- Where the $C_p$ and $\lambda^{\text{eff}}$ are the fluid thermal capacity and the thermal conductivity, respectively. In this equation, the $\lambda^{\text{eff}}$ depends on the heat conductivity of liquid and solid phase, $\lambda_{s}$ and $\lambda_l$, as the form of $\lambda^{\text{eff}} = (1-\varepsilon) \lambda_s + \varepsilon \lambda_l$ in the porous structure of electrodes. The $Q$ is the heat source term, which represents the heat generation or consumption due to various overpotential losses and chemical/electrochemical reactions. In this paper, the heat source term contains heat consumption of...
carbon gasification and heat generation of CO electrochemical reaction, H₂ electrochemical reaction, ohmic overpotential and activation overpotential.

\[ \Delta G = \Delta H - T \Delta S \]  

\( \Delta G \) is the Gibbs free energy for electricity generation which involves the ohmic overpotential and activation overpotential. \( \Delta H \) is the reaction enthalpy which is the heat consumption of carbon gasification. \( T \Delta S \) is the irreversible loss of CO electrochemical reaction and H₂ electrochemical reaction.

**Model solution and verification**

A given gas temperature is specified at the channel inlet. The outer boundary of the cathode chamber, the end of electrodes and electrolyte are thermally insulated. Inflow gas mole fraction and flow rate are given at the channel inlets. The outflow condition is specified at the outlets of the gas channels. Zero flux is specified at the end of the electrodes and pressure condition is specified at the outlets of the two gas channels. Electric potentials are specified at the two electrodes. Two ends of the cell are electrically insulated.

The model is solved at given operating conditions such as operating potential, inlet gas temperature, anode inlet gas flow rate, and the distance between carbon and anode. The output of the model includes temperature distribution, mole fraction of gas species, chemical reaction rates, and distributions of the electrochemical reaction rates in the cell. The commercial software COMSOL MULTIPHYSICS is employed for the numerical simulation.

This model is an extension of our previous model, which has already been validated with experimental data from the literature (Fig. 2(b and c)). More detailed information about the model validation can be found in Ref. [18]. In order to ensure grid-independence, six meshes of H₂O case are used for the preliminary simulations, respectively, with 30 thousand, 79 thousand, 153 thousand, 196 thousand, 237 thousand and 297 thousand cells by regulating the number of nodes. Current density and net heat generation are employed to evaluate the independence of the grids. The results are shown in Fig. 2(a). It is clear that there is a relatively large deviation between the results using the first three meshes. The numerical result of 236,777 cells has little difference with that of 297,390 cells, showing a maximum deviation of 0.14%, which is acceptable. Therefore, the mesh of 236,777 cells is used for calculations.

**Results and discussion**

**Effect of operating voltage**

The effects of operating on the current density, power density and the average cell temperature are shown in Fig. 3(a–b). The detailed operating conditions are listed in Table 5.

It is found that the performance of DC-SOFCs with H₂O as agent is much higher than that with CO₂ as agent, which is consistent with the previous study [17,18]. For DC-SOFCs with H₂O agent, the peak power density reaches 3713 W m⁻² at 0.42 V, which is more than two times of that with CO₂ agent (1395 W m⁻² at 0.56 V). The operating voltage decreases rapidly with a further increase in current density due to the huge concentration polarization. When operating potential decreases from 0.8 V to 0.1 V, the cell current density is found to increase from 831 A m⁻² to 12,308 A m⁻² for the H₂O case and from 596 A m⁻² to 2972 A m⁻² for the CO₂ case. The average cell temperature increases when the operating potential increases from 1116 K at 0.8 V to 1195 K at 0.1 V in H₂O case and from 1122 K at 0.8 V to 1154 K at 0.1 V in CO₂ case as shown in Fig. 3(b).

The significantly higher performance of H₂O-assisted DC-SOFC is due to the enhanced carbon gasification rate and the electrochemical oxidation of H₂ fuel in the anode. As can be seen in Fig. 4. In Fig. 4(a), the carbon gasification rate in H₂O assisted DC-SOFC ranges from 6.677 mol m⁻³ s⁻¹ to 25.53 mol m⁻³ s⁻¹ at 1123 K and 0.5 V operating potential. While the carbon gasification rate in CO₂ assisted DC-SOFC only ranges from 1.883 mol m⁻³ s⁻¹ to 19.4 mol m⁻³ s⁻¹. The high-value zone has obviously greater proportion in H₂O case.

The high-value zone has obviously greater proportion in H₂O case. More rapid carbon gasification kinetics by H₂O agent offers a higher mole fraction of the fuel for electrochemical reactions (both H₂ and CO). Consequently, the fuel mole fraction (CO + H₂) in H₂O case is much higher than that (CO) in CO₂.
case as shown in Fig. 4(b). In H2O case, H2 takes part in the electrochemical reaction together with CO, so that a much higher electrochemical reaction rate is obtained, which could be found from Fig. 4(c). Fig. 4(c) is a partially enlarged view of anode near the electrolyte and position at the middle of the cell. The anode electrochemical reaction rate in H2O assisted DC-SOFC ranges from \(-1.86 \text{ mol m}^{-3} \text{ s}^{-1}\) to \(4.2 \times 10^4 \text{ mol m}^{-3} \text{ s}^{-1}\) while that of CO2 assisted DC-SOFCs ranges from \(-1 \text{ mol m}^{-3} \text{ s}^{-1}\) to \(5.06 \times 10^3 \text{ mol m}^{-3} \text{ s}^{-1}\).

The temperature distribution of the DC-SOFC is shown in Fig. 5. The different temperature distribution patterns are caused by the different chemical and electrochemical processes in the DC-SOFC. In Fig. 5(a,c), it is found that the temperature increases along the cell length, the peak temperature occurs at anode/electrolyte interface and the anode chamber temperature is always lower than the cathode channel temperature, which are consistent with the result in Fig. 4, as the endothermic carbon gasification reaction takes place in the anode chamber and the electrochemical reaction takes place in the narrow region near the anode/electrolyte interface. Compared to 0.1 V, the heat generation from electrochemical reaction and overpotential losses is lower that of at 0.5 V, leading to a lower cell temperature. Compared to CO2 case, exothermic processes are greatly enhanced in H2O case due to the higher current density, which in turn increases the temperature, which could also be explained in Fig. 5(b,d) by the more significant oxygen consumption.

In order to gain a fundamental understanding of the thermal effect, Fig. 6(a,c) show a breakdown on heat consumption/generation from different components in the cell and Fig. 6(b,d) show the percentages of different heat sources. The CER represents CO electrochemical reaction, HER represents H2 electrochemical reaction, OO represents ohmic overpotential, AO represents activation overpotential, CG
represents carbon gasification and NH represents net heat of the whole cell.

More heat generation is caused by the increasing overpotential losses and electrochemical reaction rate with decreasing operating potential. On the other hand, more CO2/H2O can be generated at a higher current density, which increases the rate of the endothermic carbon gasification reaction and more heat consumption. These combined effects result in the slightly different temperature increase and net heat generation when voltage decreases, which well explains Fig. 3(b). The electrochemical reaction (CER in CO2 case and CER+HER in H2O case) contributes most to the heat generation at high potential and the contribution of ohmic overpotential and activation overpotential increases with the decreasing potential. In addition, due to the both higher heat generation and consumption compared with CO2 case, the cell temperature distribution in the H2O case is less uniform at a low operating potential, which increases the thermal stress in the cell and suffers from poor durability under changing operating potential.

As shown in Fig. 6, the net heat is changed from negative to positive when the operating voltage is decreased. The results suggest that there is thermal-neutral voltage, at which the cell is thermally self-sustained and no heat supply/removal is needed.

### Effect of anode inlet gas flow rate

The operating conditions of DC-SOFCs with both two agents are listed in Table 6. As shown in Fig. 7(a), for both H2O assisted DC-SOFC and CO2 assisted DC-SOFC, the increase of anode inlet gas flow rate has a negative effect on the cell performance. With the anode inlet gas flow rate increasing from 1 SCCM to 50 SCCM, the current density of the CO2 case decreases from 2741 A m⁻² to 2434 A m⁻². This is mainly due to the CO2 produced by electrochemical reaction is already enough for carbon gasification and the increased flowrate of

| Table 7 – Operation parameters for temperature effect study in DC-SOFCs. |
|-----------------|------------------|
| Parameters (Unit) | Value            |
| Operating potential (V) | 0.5              |
| Anode inlet gas flow rate (SCCM) | 10               |
| Cathode inlet gas flow rate (SCCM) | 400              |
| Anode gas composition for H2O/CO2 assisted DC-SOFC | 100%             |
| Cathode gas composition | Air              |
| Temperature (K) | 1073–1173        |
CO₂ will only dilute the fuel in DC-SOFC. For the H₂O case, the current density decreases from 7069 A m⁻²⁰ to 6488 A m⁻²⁰ while the anode inlet gas flow rate increasing from 1 SCCM to 50 SCCM. Although the carbon gasification rate is faster with higher flowrate of H₂O or CO₂ to produce more fuel, the temperature of both the H₂O case and CO₂ case decreases with the increasing inlet flow rate, which is shown in Fig. 7(b), as faster flow of gasification agents causes faster heat consumption of carbon gasification and takes away more heat. As the inlet gas flow rate continues to increase, the steam carbon gasification rate cannot be further increased with the increasing inlet gas flow rate. Furthermore, fuels (H₂ and CO) in anode can be also diluted by the increasing gas flow rate of H₂O or CO₂ and have less molar fractions as shown in Fig. 8(a), which results in the decrease of the current density of DC-SOFC.

Although the endothermic carbon gasification rate is much higher in H₂O case, it can be seen in Fig. 8 that the temperature of the anode chamber is higher than that in the CO₂ case, as the higher anode temperature enhances the heat transfer between the porous anode and the anode chamber. Compared with CO₂ case, it is obvious that the temperature of carbon layer near the anode increases along the cell length in the H₂O case, as more high temperature gas (H₂O/CO₂) produced by electrochemical reactions at the anode also accelerates the heat transfer.

It can be seen from Fig. 9 that the anode inlet gas flow rate only has very slight effect on heat composition both in the H₂O case and the CO₂ case. Above all, the results suggest that a high anode inlet gas flow rate is not necessary for DC-SOFC.

From the present study, it is clear that the thermal effect is significant as there could be large temperature gradient in the cell, which not only affect the performance but also the durability of the DC-SOFC.

**Effect of inlet gas temperature**

The operating conditions of DC-SOFCs at different temperatures are listed in Table 7. As can be seen from Fig. 10(a), the current density of both the H₂O case and the CO₂ case is increased at a higher temperature. Both electrochemical reaction kinetics and chemical reaction kinetics benefits from the increase of operating temperature. For the CO₂ case, with temperature increasing from 1073 K to 1173 K, the current density is greatly increased from 1151 A m⁻²⁰ to 5352 A m⁻²⁰. This substantial increase indicates that a relative higher temperature is needed for the CO₂ case as Boudouard reaction rate is quite slow at a lower temperature. For the H₂O case, the current density is 3625 A m⁻²⁰ at 1073 K, which is more than 3 times of the current density of the CO₂ case at the same temperature. This result suggests that, even at relatively lower temperature, the H₂O case still has an acceptable output power density. When the operating temperature reaches 1103 K, the current density of the H₂O case reaches 5470 A m⁻²⁰, exceeding the current density of the CO₂ case at 1173 K. Finally, the H₂O case achieves 11,369 A m⁻²⁰ at 1173 K, which is more than 2 times higher than that of CO₂ assisted DC-SOFCs. Thus, using H₂O as agent is very promising for DC-SOFC at a wider range of temperature (see Fig. 11).

In Fig. 10(b), it can be seen that there is only slight difference in average cell temperature between the H₂O case and the CO₂ case. Combining Figs. 8 and 10, it can be found that the temperature distribution difference between H₂O and CO₂ case is smaller at 1173 K than at 1073 K. This result can be explained in Fig. 12. The net heat is almost zero in most cases due to the almost same heat generation and consumption. With increasing temperature, the carbon gasification, the electrochemical reaction and the overpotential losses are all increased, which leads to thermal neutral status. The net heat in CO₂ case all remains around zero, while the net heat in the H₂O case slight increases then slight decreases with increasing temperature. This is because more H₂O and CO₂ can be generated at a higher current density at higher inlet temperature, which increases the rate of the endothermic carbon gasification and the heat consumption in the anode chamber.

**Effect of distance between carbon and anode**

Previous study has shown how the distance between carbon fuel and anode, D₇₆, have affect the performance of DC-SOFC [34]. The increase of D₇₆ will increase the variation of
Fig. 11 – Cell temperature distribution with CO₂ (a) and H₂O (b) as agents at 0.5 V and 1173 K.

Fig. 12 – Effects of anode inlet gas flow temperature on the heat compositions including CO electrochemical reaction (CER), H₂ electrochemical reaction (HER), ohmic overpotential (OO), activation overpotential (AO) and carbon gasification (CG) and net heat (NH) with CO₂ (a) and H₂O (c) as agents and percentages of different heat sources with CO₂ (b) and H₂O (d) as agents.
temperature in the cell due to different thermal conductivity between solid carbon and gas. Thus the effect of \( D_{ce} \) on the temperature distribution of the cell is discussed. Detailed operating parameters are listed in Table 8.

Table 8 — Operation parameters for \( D_{ce} \) effect study in DC-SOFCs.

<table>
<thead>
<tr>
<th>Parameters (Unit)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating potential (V)</td>
<td>0.5</td>
</tr>
<tr>
<td>Distance between anode chamber and electrode, ( D_{ce} ) (( \mu )m)</td>
<td>50—2050</td>
</tr>
<tr>
<td>Anode inlet gas flow rate (SCCM)</td>
<td>10</td>
</tr>
<tr>
<td>Cathode inlet gas flow rate (SCCM)</td>
<td>400</td>
</tr>
<tr>
<td>Anode gas composition for H(_2)O/CO(_2) assisted DC-SOFC</td>
<td>100%</td>
</tr>
<tr>
<td>Cathode gas composition</td>
<td>Air</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>1123</td>
</tr>
</tbody>
</table>

Fig. 13 shows the effects of \( D_{ce} \) on the temperature distribution in the cell with 1123 K inlet gas temperature and 0.5 V operating potential. Distance between carbon and anode surface is varied from 50 \( \mu \)m to 2050 \( \mu \)m in this study. As can be seen from Fig. 13, when \( D_{ce} \) is quite small (50 \( \mu \)m), the gradient along the cell width is small. The uniform temperature distribution is desirable to reduce the thermal stress in the cell for long-term and stable operation of DC-SOFC. With the increase of \( D_{ce} \), there occurs an obvious temperature boundary between solid carbon and anode gas channel and the gradient along the cell width becomes quite large both in \( H_2O \) and \( CO_2 \) cases. Combining Fig. 14 and Fig. 15, it can be observed that, with the increase of \( D_{ce} \), the fuel gas molar fraction in anode decreases quickly while the \( O_2 \) molar fraction in cathode channel is increasing, which means the electrochemical reaction rate and overpotential losses are decreasing, due to the increased gas transport difficulty and lower chemical reaction temperature caused by larger \( D_{ce} \). Therefore, the performance of the DC-SOFC can be decreased with the increasing \( D_{ce} \).

As stated, larger \( D_{ce} \) causes lower anode chamber temperature. However, it is found that the temperature of cell first increases and then decreases, which is due to the combination of two factors. On the one hand, larger \( D_{ce} \) weakens the heat transfer between the porous anode and the anode chamber, which tends to increase the anode temperature due to the electrochemical processes. On the other hand, the heat generation is declining with increasing \( D_{ce} \), as can be clearly seen in Fig. 16. Thus, with a further increase in \( D_{ce} \), the generated heat due to electrochemical process in the anode can no longer maintain a high temperature in the cell. Besides, it is observed from Fig. 16 that the electrochemical reaction and overpotential losses in the \( H_2O \) case are always much higher than the \( CO_2 \) case at same \( D_{ce} \), due to higher current density in the \( H_2O \) case. The percentages of overpotential losses heat account higher in \( H_2O \) case compared with \( CO_2 \) case. Above all, it is important to keep a small distance
between the carbon fuel and anode to achieve good cell performance when cell is placed horizontally.

**Conclusion**

A multi-physics model is developed to investigate the thermal effect in H$_2$O and CO$_2$ assisted tubular DC-SOFCs. The model fully considers the heat transfer, mass transport, momentum transport, chemical reactions, electrochemical reactions and transport of ions/electrons processes in the DC-SOFC. Parametric simulations are further conducted to study the effects of operating potential, the distance between carbon and anode, inlet gas temperature, and anode inlet gas flow rate on the thermal behaviors of DC-SOFC. It is found that the temperature field in DC-SOFC is highly non-uniform, which not only affect the performance but also the durability of the DC-SOFC.

Benefiting from higher cell temperature, faster carbon gasification rate, higher fuel concentration in anode and faster electrochemical reaction kinetics, DC-SOFC with H$_2$O as gasification agent performs considerably better than the DC-SOFC with CO$_2$ as gasification agent in all cases. The breakdown of heat sources of DC-SOFC shows that the H$_2$O assisted DC-SOFC has much higher heat generation and consumption than CO$_2$ assisted DC-SOFC. A thermal neutral voltage is observed, at which the cell is thermally self-sustained and no heat supply/removal is needed. High anode inlet gas flow rate is not necessary due to its slight effect on heat composition both in the H$_2$O case and the CO$_2$ case. With increasing inlet gas temperature, the net heat is almost zero in most cases due to the almost same heat generation and consumption. In addition, the distance between the anode and the carbon layer is required to be as small as possible, which benefits the improvement of the temperature uniformity and performance of the DC-SOFC.

The paper provided useful information on the thermal effects of various parts of the fuel cell along the radial direction and the general temperature trend along the length direction. Although the information of temperature and species distribution along the flow direction is provided as well, more detailed simulation and analyses are needed since the simulated cell is very short with a length of only 10 mm. Simulations of larger cells with more practical dimensions are needed for cell design and optimization. Above all, the results of this study conclusively shows that the importance of thermal effects in DC-SOFCs and form a solid foundation for DC-SOFC thermal management.
Acknowledgement

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