Modeling of Micro-Tubular Solid Oxide H$_2$O/CO$_2$ co-Electrolysis Cell for Syngas Production

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In this paper, a one dimensional chemical equilibrium co-electrolysis model is established to reveal the high temperature H$_2$O/CO$_2$ co-electrolysis process in a micro-tubular cell. The model has been roughly validated by the experimental data, systematically demonstrating the effects of current density, cell length, operating temperature and inlet gas flow rate on the products composition as well as the syngas quality. It is indicated that increasing both the electrolysis current and cell length will lead to an improved conversion rate of H$_2$O and CO$_2$ as well as an increased yield of H$_2$ and CO. High-quality syngas with 100% CO$_2$ and steam conversion rate as well as ideal H$_2$/CO ratio of 2 is achieved when the 15-cm cell is exposed to a 50-sccm cathode gas stream consisting of 56.67%H$_2$O+33.33%CO$_2$+10%H$_2$ at 800 °C and 1.0 Acm$^{-2}$. It is also found that the operating temperature, which is strongly associated with the equilibrium of reverse water gas shift reaction, plays an important role in the as-products properties. A constant H$_2$/CO ratio of 2 is achieved at 817.5 °C. Besides, reducing the inlet gas flow rate is beneficial to increase the conversion rate of H$_2$O and CO$_2$, but decrease the syngas production rate.

**Keywords:** Micro-tubular solid oxide electrolysis cell, Co-electrolysis process, Syngas production, Chemical equilibrium co-electrolysis model

1. INTRODUCTION

With fossil fuel depletion and environment deteriorating, renewable energy becomes more urgent ever before due to sustainability and non-pollution[1, 2]. As the contribution of renewable energies such as wind, solar, biomass, etc. to electricity grids increase[3-5], the misalignment between the intermittency of renewables and the dynamics of power demand becomes more acute, resulting in increased challenges in grid management[6, 7]. Therefore, large-scale energy conversion and storage with higher efficiency is indispensable in a sustainable energy system. Meanwhile, Global warming due to high greenhouse gases level requires more effective strategies to capture and store CO$_2$[8, 9].
Solid oxide co-electrolysis cell (Co-SOEC) is a promising electrical-to-chemical energy conversion device to produce syngas (a mixture of H₂ and CO) by H₂O/CO₂ splitting[8-17]. The produced syngas can be subsequently used as the feedstock of the Fischer-Tropsch (F-T) reaction to produce synthetic liquid fuels, which exhibit high energy density and are able to use the current fundamental infrastructure for storage and transportation without extra investment. As a result, the synthetic liquid fuels have been proposed as an alternative to fossil fuels[18]. Steam and CO₂ could be electrolyzed separately and mixed together to produce syngas. However, the sole CO₂ electrolysis process shows a significantly slow kinetic reaction rate, resulting from the high polarization resistance. Moreover, sole CO₂ electrolysis could also has a high risk of coking by the deep electrolysis of CO to C. Therefore, it has great advantages to produce syngas by the steam/CO₂ co-electrolysis reaction, due to the improved energy efficiency and less potential of coking[19, 20].

High temperature steam/CO₂ co-electrolysis process performed on solid oxide cells (SOCs) are much complex, which involves the electrochemical reactions and a reverse water gas shift (RWGS) reaction[19]. During the co-electrolysis process, H₂O and CO₂ accept electrons from an external circuit to produce H₂, CO and oxygen ions (O²⁻) at the cathode, and then the oxygen ions are pumped from the cathode side to the anode side through the dense electrolyte, and then released electrons to form oxygen gas. Besides the electrochemical reactions at both electrodes, the RWGS reaction can also occur in the cathode side at the same time in a kinetically fast rate. It is believed that the water splitting reaction is responsible for the H₂ production, while the RWGS reaction plays a dominant role in the CO formation. Because the sole CO₂ electrolysis reaction occurs in a relatively slow kinetics resulting from the high polarization resistance and low electrolysis current density. Electrochemical performance have been measured on the same solid oxide cell in three different modes including sole steam electrolysis, CO₂ electrolysis and co-electrolysis[19]. The cells, consisting of Ni-YSZ/YSZ/YSZ-LSM, exhibited an area specific resistance (ASR) of 1.38 Ωcm² in the co-electrolysis mode, much comparable to 1.36 Ωcm² in the sole steam electrolysis, but only 36% of 3.84 Ωcm² for sole CO₂ electrolysis. Similar results showing comparable electrochemical performance of co-electrolysis to steam electrolysis process are also reported by Graves et al. and Chen et al.[21, 22], further indicating the participation of RWGS reaction. Therefore, the high temperature steam/CO₂ co-electrolysis is a simultaneously synergistic process of electrochemical steam splitting reactions and RWGS reaction.

The addition of RWGS reaction has brought much complexity to the solid oxide co-electrolysis process. On one hand, the inlet gases properties such as gas fractions and mass flow rate have great effects on the oxygen partial pressure and gas transport properties, which are strongly related to the electrochemical performance of the cells. On the other hand, unlike the clearly linear relationship between the gas production rate and the electrolysis current in the sole steam or CO₂ electrolysis, it is no longer sufficient to use the Faraday’s law to evaluate the syngas products properties, which are greatly important for the downstream F-T reaction to determine whether it needs reforming or not. A series of models have been developed to better understand the electrochemical process in a solid xode co-electrolyzer, design cell microstructure and optimize the operation conditions[19, 23-29]. For instance, Stoots et al. and Wang et al. have reported and validated the chemical equilibrium co-electrolysis model to evaluate the outlet gases composition of high temperature steam/CO₂ co-
electrolysis process operated on the planar solid oxide electrolysis cells [19, 26, 30]. It is reported that high-quality syngas with the H2/CO ratio close to 2, and 100% CO2 conversion to CO have been produced when the planar cell stacks were exposed to the cathode gas stream consisting of 10.2%H2-12.4%CO2-61.9%N2-15.5%H2O at 800 ºC and 13 A. Luo et al. developed a two-dimension electro-thermal model to reveal the effects of operating temperature, cell voltage, inlet gas mass flow rate and fractions on the energy efficiency, electrolysis current and products fractions in a regular tubular SOEC with the inner diameter of 8.5 mm[28, 29]. It is found that the energy efficiency of 59.4% as well as the conversion rate of 48.3% were achieved when the cells were exposed to a gas stream consisting of 50%H2O-50%CO2 at 700 ºC and 1.4 V. Therefore, these models have revealed the effects on operating conditions to the syngas production, and the results offered valuable guidance to produce high-quality syngas via co-electrolysis process.

As we all know that the SOCs for high temperature co-electrolysis reaction could be in forms of either planar or tubular configuration, and the former configuration has been widely studied in the field of SOCs[23-29]. Compared with the planar SOCs, tubular SOCs have great advantages of higher mechanical/thermal stability and easier seal requirements. However, the current densities achieved on tubular SOCs are not yet comparable to those with planar SOCs due to the imperfect current collector. The micro-tubular SOCs, especially with the tube diameter lower than 2 mm, are subsequently developed, which combine both planar and tubular structures advantages, showing enhanced volumetric power densities as well as faster start-up properties[31-39]. Up to now, the studies about high temperature steam/CO2 co-electrolysis process on micro-tubular SOCs are still rare. Therefore, in this work, we are supposed to report a one-dimensional (1D) numerical chemical equilibrium co-electrolysis model to reveal the effects of current density, cell length, operating temperature and cathode inlet gas flow rate on the gas composition in the micro-tubular co-electrolyszer. The effects of operating conditions on the syngas qualities are also discussed.

2. MODEL DEVELOPMENT

2.1. Reaction scheme for H2O/CO2 co-electrolysis

A solid oxide co-electrolysis cell is composed of two porous electrodes and a thin electrolyte film, in which the two porous electrodes are typically made of Ni-YSZ (as the cathode) and LSM-YSZ (as the anode), respectively, while the electrolyte is normally made of the oxygen conducting YSZ. The whole high temperature steam/CO2 co-electrolysis reaction performed on the solid oxide cells can be expressed as the following:

\[
\text{Cathode: } \text{CO}_2(g) + 2e^- \rightarrow \text{CO}(g) + O^{2-} \tag{1}
\]
\[
\text{H}_2\text{O}(g) + 2e^- \rightarrow \text{H}_2(g) + O^{2-} \tag{2}
\]
\[
\text{Anode: } 2O^{2-} \rightarrow O_2(g) + 4e^- \tag{2}
\]

Therefore, the overall high temperature co-electrolysis reaction occurred on solid oxide cells can be expressed as Eq. (3):

\[
\frac{m\text{CO}_2(g) + n\text{H}_2\text{O}(g)}{\text{Cathode side}} \xrightarrow{\text{Electricity+Heat}} \frac{m\text{CO}(g) + n\text{H}_2(g)}{\text{Anode side}} + \frac{m+n}{2} \text{O}_2(g) \tag{3}
\]
Where the syngas is produced in the cathode side in combination with CO\(_2\) and H\(_2\)O, and oxygen gas is produced in the anode side as a by-product. In addition to the electrochemical reaction, RWGS reaction occurs with a fast kinetic rate in the cathode side at high temperature as shown in Eq. (4):

\[
\text{CO}_2(g) + \text{H}_2(g) \leftrightarrow \text{CO}(g) + \text{H}_2\text{O}(g)
\]  \hspace{1cm} (4)

Steam and CO\(_2\) are split into H\(_2\) and CO in the cathode side, where the reducing gases of CO or H\(_2\) are required to prevent the oxidation of Ni. As a result, RWGS reaction are inevitably occurred in the meantime. The whole cathode reaction could be seen as the reunion of the H\(_2\)-CO-H\(_2\)O-CO\(_2\).

2.2. Model assumptions

The present model of the micro-tubular Co-SOEC is schematically shown in Figure 1. In a micro-tubular co-electrolyzer, steam and CO\(_2\) are co-supplied to the lumen side of micro-tubular cell while the atmosphere air is fed into the shell side. To simulate the reactions in the co-electrolysis mode, the main model assumptions are shown as follows:

1. All gases are assumed to be ideal gases, and the gas flow in the core of the cell is assumed to uniform to the plug flow model.

2. The cell operating temperatures monitored by the thermocouple and controlled by the furnace could be considered to be uniformly distributed.

3. Not only the distribution of electronic and ionic conductors in the electrodes (cathode and anode), but also the microstructures of the electrodes are assumed to be uniform and continuous.

4. Methanation reaction in the cathode side is neglected due to the significantly low methane concentration formed in the co-electrolysis reaction zone as reported by Xie et al.\[11\], while carbon formation can be remarkably suppressed due to high steam concentration \[19\]. The electrochemical process is dominated by water electrolysis while CO is assumed to be produced only by the subsequent RWGS reaction.

5. The convection diffusion in the porous electrodes caused by pressure gradient as well as the radial concentration gradient of gases is ignored.

6. The heterogeneous chemical and electrochemical reactions in the cell unit as well as the mean field approximation are applied in the each segment of the cell (Figure 1B).

Figure 1. Schematic evolution of the gas composition in the cathode side of a micro-tubular H\(_2\)O/CO\(_2\) co-electrolysis cell, A) the entire cell, B) the ith segment of the cell.
2.3. Model description and solution

As shown in Figure 1A, the micro-tubular Co-SOEC is divided into \( n \) identical units and each unit is 0.01 cm length, which occur the RWGS reaction and the subsequent electrolysis reaction during the co-electrolysis operation. The \( y_{i,ax} (x=\text{H}_2\text{O}, \text{CO}_2, \text{H}_2, \text{CO}) \) represents the molar fraction of the \( i^{\text{th}} \) unit at the inlet of the RWGS stage, that can be known from the outlet gas composition of the previous unit (the \((i-1)^{\text{th}}\) unit), while \( y_{i,ax}' (x=\text{H}_2\text{O}, \text{CO}_2, \text{H}_2, \text{CO}) \) represents the molar fractions of the same compounds after RWGS reaction. Three mass balance equations for C, H, and O elements can be written as Eqs. (5)-(7).

\[
y_{i,\text{CO}_2} + y_{i,\text{CO}} = y_{i,\text{CO}_2}' + y_{i,\text{CO}}' \quad (5)
\]

\[
y_{i,\text{H}_2} + y_{i,\text{H}_2} = y_{i,\text{H}_2}' + y_{i,\text{H}_2}' \quad (6)
\]

\[
2y_{i,\text{CO}_2} + y_{i,\text{CO}} + y_{i,\text{H}_2} = 2y_{i,\text{CO}_2}' + y_{i,\text{CO}}' + y_{i,\text{H}_2}' \quad (7)
\]

\[
K(T) = \frac{y_{i,\text{CO}_2}'y_{i,\text{H}_2}'}{y_{i,\text{CO}_2}y_{i,\text{H}_2}} \quad (8)
\]

\[
\ln \left( K^{-1} \right) = -2.4198 + 0.0003855 \times T + 2180.6/T \quad (9)
\]

The Eq. (8) shows the relationship between the equilibrium constant \( (K) \) of RWGS reaction and the equilibrium molar fractions of four chemical compounds (CO, CO\(_2\), H\(_2\) and H\(_2\)O). Since the constant is temperature-dependent, an empirical equation (Eq. (9)) is employed to link the equilibrium constant and the operating temperature \( (T) \)[40]. Therefore, the resulting system can be solved with five equations and five unknowns.

The gas composition after the co-electrolysis stage shown in Figure 1B, \( y_{i+1,ax} (x=\text{H}_2\text{O}, \text{CO}_2, \text{H}_2, \text{CO}) \), can be calculated similarly, but the mass balance equation for oxygen must be modified to account for oxygen removal from cathode to anode, as shown in Eqs. (10)-(13).

\[
y_{i+1,\text{CO}_2} + y_{i+1,\text{CO}} = y_{i+1,\text{CO}_2} + y_{i+1,\text{CO}} \quad (10)
\]

\[
y_{i+1,\text{H}_2} + y_{i+1,\text{H}_2} = y_{i+1,\text{H}_2} + y_{i+1,\text{H}_2} \quad (11)
\]

\[
2y_{i+1,\text{CO}_2} + y_{i+1,\text{CO}} + y_{i+1,\text{H}_2} = 2y_{i+1,\text{CO}_2} + y_{i+1,\text{CO}} + y_{i+1,\text{H}_2} + \Delta n_0 \quad (12)
\]

\[
K(T) = \frac{y_{i+1,\text{CO}_2}y_{i+1,\text{H}_2}}{y_{i+1,\text{CO}_2}'y_{i+1,\text{H}_2}'} \quad (13)
\]

According to the Faraday’s law, the molar fraction of the transferred oxygen ions, \( \Delta n_0 \), is proportional to the electrical current, as shown in Eq. (14).

\[
\Delta n_0 = \frac{I_A}{2FN_{\text{tot}}} \quad (14)
\]

where \( I_A \) is the electrical current (electrolysis current), \( N_{\text{tot}} \) is the total molar flow rate at the cathode side and F is the Faraday’s constant. In general, determination of the gas composition in every unit is an iterative process.

The model is solved by setting a certain electrolysis current density, cell length, operating temperature or inlet gas flow rate. The outputs of the model are the distributions of species gas fraction, molar ratio of H\(_2\) to CO and others. The calculations are performed using the commercial software MATLAB.
3. RESULTS AND DISCUSSION

3.1. Model validation

The model is validated by comparing the measured current density-cell voltage \((i-V)\) curves with the simulated results. As expressed in Eq. (15), the cell voltage is determined by the open circuit voltage (OCV) and over-potential resulting from electrical loss including activation, ohmic, and concentration polarization\[41, 42\].

\[
V_{OP} = V_N - i \times ASR(T)
\]  

(15)

where \(ASR(T)\), area-specific resistance, a temperature-dependent parameter, which quantifies the cell performance loss during Co-SOEC operation, can be estimated and determined by experimental data or an appropriate model.

According to the modeling results\[41, 42\], once the equilibrium gas composition are determined, the OCV of the solid oxide cells at a given operating temperature could be calculated by using the Nernst equation in Eq. (16)\[43\],

\[
V_N = -\frac{\Delta G_{f,H_2O}^o(T)}{2F} - \frac{RT}{2F} \ln \left( \frac{\gamma_{i,H_2O}^0}{\gamma_{i,CO_2}^0 \gamma_{i,CO}^{0.5}} \right)
\]

(16)

where \(\Delta G_{f,H_2O}^o(T)\) and \(\Delta G_{f,CO_2}^o(T)\) are the change of Gibbs free energy for \(H_2O\) and \(CO_2\) formation reactions, respectively, \(R\) is the universal gas constant, and \(\gamma_{O_2}^0\) is the oxygen partial pressure in the anode side, a constant of 0.21 when the anode is exposed to the ambient air.

Table 1. Operation conditions of micro-tubular \(H_2O/CO_2\) co-electrolysis cell reported by Kleiminger et al. [32].

<table>
<thead>
<tr>
<th>Gas flow rates in the electrodes (sccm)</th>
<th>Parameters (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>CO₂</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 1 lists a series of operating parameters identical to the value reported by Kleiminger et al. [32], to make the simulation including inlet gas composition, operating temperature and ASR at OCV. The simulated results are shown in Figure 2, which has good agreements with the measured \(i-V\) curves in the whole range of current densities, indicating that the 1D chemical equilibrium co-electrolysis model proposed here is feasible to reveal the high temperature steam/\(CO_2\) splitting reaction in micro-tubular Co-SOEC.
Figure 2. Modeling and experimental polarization curves of H$_2$O/CO$_2$ co-electrolysis at 822 °C.

3.2. Effect of electrolysis current

Figure 3. A) CO$_2$ molar fraction, B) CO molar fraction, C) H$_2$O molar fraction, D) H$_2$ molar fraction, and E) molar ratio of H$_2$ to CO for the product stream as functions of electrolysis current density and cell length in a micro-tubular co-electrolyzer at 800 °C with an inlet gas flow rate of 50 sccm at the cathode inlet, predicted by the chemical equilibrium model.
It is well known that the electrolysis current \( (I_A) \) can be expressed as

\[
I_A = i_A \times A
\]  

(17)

in which the effective electrolysis area \( (A) \) can be given by

\[
A = \pi \times d \times l
\]  

(18)

where \( d \) and \( l \) are the diameter and length of the micro-tubular co-electrolyzer, respectively. As a result, \( A \) is directly proportional to \( l \) at a fixed \( d \) value. Therefore, in this work, \( I_A \) is directly associated with cell length \( (l) \) and electrolysis current density \( (i_A) \) as \( d \) is set to be a constant of 0.136 cm, and thus the electrolysis current \( (I_A) \) effect on the \( \text{H}_2\text{O}/\text{CO}_2 \) co-electrolysis system can be directly studied by varying the cell length \( (l) \) or/and electrolysis current density \( (i_A) \).

Figure 3 A-D show the products fractions at 800 °C along the micro-tubular Co-SOEC’s main flow stream as functions of the cell length \( (l) \) and electrolysis current density \( (i_A) \), when the cells are exposed to a gas stream composed of 56.67%H\textsubscript{2}O-33.33%CO\textsubscript{2}-10%H\textsubscript{2}. The molar fractions of CO and H\textsubscript{2} at a given position also increase with increasing the electrolysis current density, especially H\textsubscript{2} (Figure 3B and D), for example, for a 15cm-length micro-tubular cell, the molar fraction of H\textsubscript{2} and CO at 800 °C has increased from 26.94% and 12.60% at 0.25 A cm\textsuperscript{-2}, to 47.16% and 21.92% at 0.5 A cm\textsuperscript{-2}, respectively. Accordingly, the conversion rate of H\textsubscript{2}O and CO\textsubscript{2} has increased from 29.89 % and 37.80 % to 65.59 % and 65.74 %, respectively. Because the molar flow rate of oxygen ions transferred from the cathode is proportional to the electrolysis current, the increment of electrolysis current density as well as cell length suggests an increased molar rate of H\textsubscript{2} from water splitting. The produced H\textsubscript{2} subsequently promote the RWGS reaction moving to the direction for producing CO. Therefore, increasing the electrolysis current density is beneficial to promote syngas production. Moreover, it should be noticed that the steam and CO\textsubscript{2} would be completely converted into syngas when the electrolysis current comes up to the critical value, \( I_c \). \[19, 30\]

\[
I_c = 2 \times F \times (n_{\text{H}_2\text{O}} + n_{\text{CO}_2})
\]  

(19)

where \( n_{\text{H}_2\text{O}} \) and \( n_{\text{CO}_2} \) are the inlet molar flow rate of H\textsubscript{2}O and CO\textsubscript{2} in the cathode, respectively. Further increasing the electrolysis current would possibly result in coking by a deep electrolysis of CO to C\[19, 20, 44\]. Meanwhile, the unnecessary high electrolysis current is unfavorable to reduce the energy efficiency and generate extra heat for electrode degradation. According to the results of gas composition in Figure 3A-D, the molar ratio of H\textsubscript{2} to CO as a function of current density could be calculated along the longitudinal direction of the micro-tubular cell. It could be seen from Figure 3E that the molar ratio of H\textsubscript{2} to CO slightly increase at the beginning, but subsequent decrease with increasing the electrolysis current. When a 15-cm micro-tubular Co-SOEC is exposed to a 50 sccm (standard cubic centimeters per minute) cathode gas stream consisting of 56.67%H\textsubscript{2}O+33.33%CO\textsubscript{2}+10%H\textsubscript{2} at 800 °C, the molar ratio of H\textsubscript{2} to CO slightly increases from 2.14 at 0.25 A cm\textsuperscript{-2} to 2.15 at 0.5 A cm\textsuperscript{-2}, but sharply decreases to 2.00 at 0.82 A cm\textsuperscript{-2}. The results could be explained by different routines of producing syngas, where H\textsubscript{2} is originated from water electrolysis while CO is primarily produced by RWGS reaction. As the steam is easier to be split to H\textsubscript{2} prior to CO\textsubscript{2} splitting to CO, the molar ratio of H\textsubscript{2} to CO has increased up to 2.165 when the steam is totally reduced. However, the subsequent RWGS reaction for CO formation results in a increase of CO fraction, and further a rapid reduction of H\textsubscript{2}/CO to 2.
3.3. Effect of operating temperature

Figure 4 A-D show the effect of operating temperature on the products fraction along the length direction of a 15-cm micro-tubular Co-SOEC, which is exposed to a 50 sccm gas stream composed of 33.33%CO$_2$+10%H$_2$+56.67%H$_2$O. With the operating temperature increasing from 700 to 900 °C, the molar fraction of CO at the position of 10 cm has increased from 12.0% to 21.3%, while the value of H$_2$ has decreased from 37.4% to 28.1%. The opposite effects of operating temperature on CO and H$_2$ production could be explained by an increased equilibrium constant of the RWGS reaction, which are 0.633, 0.944, 1.0 and 1.302 at 700, 800, 817.5 and 900°C, respectively. Consequently, increasing the operating temperature could promote the RWGS reaction, which is beneficial to CO formation by consuming H$_2$, and the similar results have been reported by Stoots et al. [19, 38] and Wang et al.[39, 45].

![Figure 4](image)

Figure 4. A) CO$_2$ molar fraction, B) CO molar fraction, C) H$_2$O molar fraction, D) H$_2$ molar fraction, and E) molar ratio of H$_2$ to CO for the product stream as a function of the operating temperature in a 15-cm-length micro-tubular co-electrolyzer under the electrolysis current density of 0.5 A cm$^{-2}$ and an inlet gas flow rate of 50 sccm at the cathode inlet, predicted by the chemical equilibrium model.
The information of the overall gas composition are exhibited in Figure 5A to further reveal the operating temperature effect on the co-electrolysis process. The open circles in the y axis represent the cold inlet molar fractions, which inevitably change due to the re-equilibrium of the RWGS reaction at different operating temperatures. For instance, the initial inlet molar fraction of H₂ is 10%, it decreases to 7.61%, 6.83%, 6.69% and 6.06% at 700, 800, 817.5 and 900 °C, respectively. On the contrary, the initial inlet molar fraction of CO is 0, it increases to 2.43%, 3.21%, 3.35% and 3.98%. The opposite temperature effect on the molar fraction of H₂ and CO is possibly attributed to different production routines as mentioned above, which can also be confirmed by the experimental results performed on a ten-cell stack and reported by Stoots et al. in Idaho National Laboratory [19, 38].

According to the results of gas fraction in Figure 4A-D, the molar ratio of H₂ to CO is also calculated to evaluate the temperature effect on the syngas quality. It is shown in Figure 4E and Figure 5 that the molar ratio of H₂ to CO at the same position has decreased with increasing the operating temperature, since it is beneficial to the RWGS reaction for CO formation by consuming H₂[19, 38, 39, 45, 46]. Furthermore, it is known from Eqs.(8) and (13) that the molar ratio of CO to CO₂ is \( K \) times that of H₂ to H₂O. At 817.5 °C, the equilibrium constant, \( K \), equals to a special value of 1, which indicates the conversion rate of CO₂ is identical to that of H₂O. Therefore, the molar ratio of H₂ to CO is stable with a constant value of 2 along the length direction of the micro-tubular Co-SOEC. In the case of operating temperature lower than 817.5 °C with \( K<1 \), the conversion rate of CO₂ is lower than that of H₂O, suggesting that H₂O would be totally converted prior to CO₂. Consequently, the molar ratio of H₂ to CO higher than 2 are achieved. Similarly, in the case of operating temperature higher than 817.5 °C with \( K>1 \), the conversion rate of CO₂ is higher than that of H₂O, resulting in a molar ratio of H₂ to CO lower than 2. Therefore, it needs appropriate operating temperature to produce high-quality syngas as the ideal feedstock of F-T reaction via co-electrolysis process in a micro-tubular Co-SOEC.

Figure 5. A) Molar fraction and B) molar ratio of H₂ to CO for the product stream along the longitudinal direction in a 15-cm-length micro-tubular co-electrolyzer at 700, 800, 817.5 and 900 °C, under the electrolysis current density of 0.5 A cm⁻², with a gas flow rate of 50 sccm at the cathode inlet, predicted by the chemical equilibrium model.
3.4. Effect of inlet gas flow rate

Figure 6 A-D show the effect of the inlet gas flow rate on the products fraction along the length direction of a 15-cm micro-tubular Co-SOEC, which is exposed to the cathode gas stream composed of 33.33\%CO₂+10\%H₂+56.67\%H₂O. The molar fractions of CO and H₂ as well as the conversion rates of CO₂ and H₂O decrease with increasing the inlet gas flow rate. Since the electrolysis current density is constant, it indicates that the molar flow rate of oxygen ions transferred from the cathode to the anode remains the same. In this case, the increase of the total inlet gas molar flow rate would lead to a reduced fraction of individual gas, and further a low reactant utilization, which has also been reported by previous literatures \[32, 47\]. The total minimum molar flow rate of H₂O and CO₂ should be not less than \( \frac{I}{2F} \), as described in Eq. (20).

\[
n_{\text{H}_2\text{O}} + n_{\text{CO}_2} \geq \frac{I}{2F} \tag{20}\]

Otherwise, the insufficient supply of oxygen in the cathode side would lead to coking by the deep splitting of CO to C[19, 20, 44, 48], which will occupy the active reaction sites of the electrodes and result in the reduction of three phase boundaries and further cell degradation. Therefore, the inlet gas molar flow rate should match well with the electrolysis current in perspective of reactant utilization and cell durability\[32, 47\].

Figure 6. A) CO₂ molar fraction, B) CO molar fraction, C) H₂O molar fraction, D) H₂ molar fraction, and E) molar ratio of H₂ to CO for the product stream as a function of inlet gas flow rate on the 15-cm micro-tubular co-electrolyzer at 800 °C under the electrolysis current density of 0.5 A cm⁻², predicted by the chemical equilibrium model.
Once the gas fractions of H₂ and CO are determined, the molar ratio of H₂ to CO as a function of the inlet gas flow rate is evaluated and shown in Figure 6E. An ideal H₂/CO ratio of 2 as well as complete conversion of CO₂ and H₂O can be achieved at the low inlet gas flow rate. Subsequently, with increasing the inlet gas flow rate, the molar ratio of H₂ to CO sharply increases while CO₂ conversion ratio significantly decreases. The results are attributed to the higher conversion rate of H₂O than that of CO₂, evaluating from \( K < 1 \) at 800 °C. The maximum H₂/CO ratio of 2.163 is obtained when H₂O is basically electrolyzed to H₂ at a critical inlet gas flow rate, calculated by Eq. (20). At this time, further increasing the inlet gas flow rate causes the molar ratio of H₂/CO gradually decreasing to 2.124. Therefore, the inlet gas flow rates should be compatible to the electrolysis current to produce high-quality syngas for the F-T reaction.

4. CONCLUSIONS

1D numerical chemical equilibrium co-electrolysis model is developed to reveal the effects of the operating conditions including the electrolysis density, cell length, operating temperature, and the inlet gas flow rate on the outlet gas composition as well as the syngas quality. The model has been validated by the good agreement of the simulated results with the measured i-V curves. It is found that increasing the electrolysis current density or cell length is beneficial to increase the yield of H₂ and CO as well as the conversion rates of H₂O and CO₂ in the cathode side. The operating temperature has a great influence on the equilibrium constant of reverse water gas shift (RWGS) reaction, and further the outlet gas fractions. A constant molar ratio of H₂ to CO of 2 is achieved at 817.5 °C. Moreover, reducing the inlet gas flow rate is beneficial to increase the conversion rate of H₂O and CO₂, but decrease the syngas production rate. Therefore, appropriate electrolysis current density, cell length, operating temperature and inlet gas flow rate are required to produce high-quality syngas with ideal H₂/CO ratio and high conversion rate using the micro-tubular Co-SOECs.

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