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Syngas Production by High Temperature Steam/CO₂ Coelectrolysis Using Solid Oxide Electrolysis Cells

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Abstract

High temperature (HT) steam/CO₂ coelectrolysis with solid oxide electrolysis cells (SOECs) using the electricity and heat generated from clean energies is an important alternative for syngas production without fossil fuel consumptions and greenhouse gas emissions. Herein, reaction characteristics and outlet syngas composition of HT steam/CO₂ coelectrolysis under different operating conditions, including distinct inlet gas compositions and electrolysis current densities, are systematically studied at 800°C using the commercially available SOECs. The HT coelectrolysis process, which has comparable performance to HT steam electrolysis, is more active than the HT CO₂ electrolysis process, indicating the important contribution of the reverse water-gas shift reaction in the formation of CO. The outlet syngas composition from HT steam/CO₂ coelectrolysis is very sensitive to the operation conditions, indicating the feasibility of controlling the syngas composition by varying the operating conditions. A maximum steam and CO₂ utilization of 77% and 76% is achieved at 1.0 A cm⁻² with an inlet gas composition of 20% H₂ / 40 %

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1. Introduction

Recently, HT steam/CO\textsubscript{2} coelectrolysis using SOECs, which electrochemically electrolyze CO\textsubscript{2} and steam into syngas (CO+H\textsubscript{2}), provides an alternative to the traditional syngas production technologies including coal gasification and natural gas reforming, which release a lot of greenhouse gases and cause serious environmental concerns\textsuperscript{1-4}. It is also highly valued as a crucial and limiting step in the CO\textsubscript{2} recycling process including CO\textsubscript{2} capture, dissociation and reuse due to its improved stability by reducing the possibility of carbon deposition associated with HT CO\textsubscript{2} electrolysis\textsuperscript{5,6}. When coupled with clean energies, such as solar, wind and nuclear energies, HT steam/CO\textsubscript{2} coelectrolysis can store the generated heat and power in the form of chemical energies in syngas that can be further processed into liquid fuels like synthetic diesel or dimethyl ether (DME) via catalytic reactions, thereby resolving the related energy storage issues as well as the supply-and-demand conflicts\textsuperscript{7,8}. Therefore, the development of HT coelectrolysis technologies bears great significance for the large-scale application of clean energies and reduction of CO\textsubscript{2} emissions.

Christopher Graves\textsuperscript{9} et al. have made a review of different routes for steam/CO\textsubscript{2} dissociation, including thermolysis, thermochemical cycles,
electrolysis and photoelectrolysis, concluding that HT steam/CO$_2$ coelectrolysis with SOECs is the most efficient path with a potential electricity-to-syngas efficiency of $\sim$100%. The process model established by Carl M. Stoots$^{10}$ at Idaho National Lab (INL) predicts an overall thermal-to-syngas efficiency of 48.3 ± 5.0% for large-scale HT steam/CO$_2$ coelectrolysis. Qingxi Fu$^5$ et al. have made an economic analysis of synthetic fuel production by using the syngas produced from HT steam/CO$_2$ coelectrolysis and the diesel production cost is estimated to be 0.86€/l, comparable to that of the biomass-to-liquid process. Therefore, HT steam/CO$_2$ coelectrolysis is a promising technology for syngas production with high efficiency and feasibility.

Compared with HT steam or CO$_2$ electrolysis, the study on HT steam/CO$_2$ coelectrolysis is much more complicated and the reasons include: (1) apart from electrochemical reactions (equation 1-2), the chemical reaction of reverse water-gas shift reaction (RWGS, equation 3) also plays an important part in the formation of CO; (2) the equilibrium of the RWGS is highly sensitive to the outlet gas temperature from the electrolysis cell; and (3) the performance and syngas composition change significantly with the microstructure of SOECs and the operation conditions$^{11-13}$. It also explains why tremendously different phenomena have been observed by different groups.

\[
\begin{align*}
H_2O (g) & \xrightarrow{electricity} H_2 (g) + 1/2 O_2 (g) \quad (1) \\
CO_2 (g) & \xrightarrow{electricity} CO (g) + 1/2 O_2 (g) \quad (2)
\end{align*}
\]
\[
\text{CO}_2 (g) + \text{H}_2 (g) \rightarrow \text{CO} (g) + \text{H}_2\text{O} (g) \quad (3)
\]

Up to now, the information available on HT steam/CO\textsubscript{2} coelectrolysis is very limited and previous studies primarily focus on novel materials development, performance characterization, and system efficiency analysis\textsuperscript{14-18}. A number of fundamental questions still need to be answered. For example, the contribution of RWGS in the HT coelectrolysis process is still unclear. Carl M. Stoots \textsuperscript{19} et al. report an area specific resistance (\textit{ASR}) of 1.38 \(\Omega\) cm\textsuperscript{2} for HT coelectrolysis at 800\(^\circ\)C, close to that 1.36 \(\Omega\) cm\textsuperscript{2} for HT steam electrolysis and much lower than that of 3.84 \(\Omega\) cm\textsuperscript{2} for HT CO\textsubscript{2} electrolysis, concluding that CO during HT steam/CO\textsubscript{2} coelectrolysis is primarily formed via the RWGS reaction. Nevertheless, M. Mogensen \textsuperscript{1} and Zhongliang Zhan \textsuperscript{20} et al. report similar \textit{ASR} values with small difference for SOECs under the three different modes, inconsistent with the results of Carl M. Stoots et al.. Another issue regarding the relationship between the outlet syngas composition and the inlet gas composition, which can provide useful information on the control of the syngas composition, is still scarcely studied. Herein, a systematic study is conducted on HT steam/CO\textsubscript{2} coelectrolysis using the commercially available SOECs from Ningbo Institute of Industrial Technology to evaluate the performance, reaction characteristics, outlet gas composition and steam/CO\textsubscript{2} utilization of HT steam/CO\textsubscript{2} coelectrolysis under different operation conditions, including different inlet gas compositions and electrolysis current densities.

2. Experimental
All the button cells and single cells used in this study are purchased from Ningbo Institute of Industrial Technology. The SOECs are cathode-supported cells composed of Ni-YSZ (Y$_2$O$_3$-doped ZrO$_2$) cathode/YSZ electrolyte/ GDC (Gd$_2$O$_3$-doped CeO$_2$) buffer layer/ LSCF ((La$_{0.6}$Sr$_{0.4}$)(Co$_{0.2}$Fe$_{0.8}$)O$_3$) anode. The button cells are ~2.4 cm in diameter with an active area of 1 cm$^2$ at the anode side. A single cell (10×10 cm$^2$) with an active area of 64 cm$^2$ after the application of sealant is used during the study on the effect of the inlet gas composition on the performance and outlet gas compositions under a constant electrolysis current density of 0.15 A cm$^{-2}$. A single cell (5×5 cm$^2$) with an active area of 16 cm$^2$ is used during the study on the influence of electrolysis current densities on the HT steam/CO$_2$ coelectrolysis between 0-1.0 A cm$^{-2}$ considering the upper current limit of 22 A of the electrochemical workstation. The cross-section SEM image and photo of the single cell is shown in Fig.1.

A schematic of the apparatus used for HT steam/CO$_2$ coelectrolysis analysis is shown in Fig.2. The system is primarily composed of the corresponding gas bottles, mass flow controllers (MFC), a bubbler as the humidifier, humidity indicator (H), pressure gauges (P), thermometers (T), high temperature furnace, the solid oxide electrolysis cell, the dehumidifier to remove the steam in the outlet gas by cooling, the volumetric flow meter, and the Agilent 7820A gas chromatography (GC). H$_2$ is supplied to the single cell at a flow rate of 300 sccm for the reduction of the NiO particles in the cathode prior to the HT electrolysis measurements. In order to prevent the partial oxidation of the Ni particles in the
cathode, 20 mol. % of H₂ is used as the protection gas. In the anode, air is used as a sweeping gas at a flow rate of 300 sccm. CO₂ and H₂ at selected flow rate are controlled by the mass flow controller and directed into the humidifier to be mixed with the steam, whose content is changed and controlled by the water temperature in the humidifier. The accurate steam content is calculated and calibrated by the total pressure and humidity indicator placed at the exit of the humidifier via equation (4) below:

\[ C_{s,i} = \frac{p_s H}{P_t} \]  

(4)

where, \( C_{s,i} \) is the steam content in the inlet gas, \( H \) is the relative humidity measured by the humidity indicator, \( p_s \) is the corresponding saturated steam pressure at the measured temperature and pressure, \( p_t \) is the total pressure measured by the pressure gauge. The flow rate of steam (\( Q_{s,i} \)) under the normal conditions is determined by equation (5):

\[ Q_{s,i} = C_{s,i} (Q_{CO2,i} + Q_{H2,i}) / (1 - C_{s,i}) \]  

(5)

where, \( Q_{CO2,i} \) and \( Q_{H2,i} \) is the corresponding flow rate of CO₂ and H₂ controlled by the mass flow controller. During the button cell test, the total flow rate (\( Q_t \)) of the inlet gas is fixed at 100 sccm for the button cell test and 200 sccm for the single cell test. The temperature of the mixed gas from the humidifier is further elevated to \( \sim 150^\circ \text{C} \) and a layer of heat insulating materials is applied outside the gas channel to avoid steam condensation, as indicated by the dashed line in Fig.2. The inlet gas is then directed into SOEC for HT coelectrolysis. The input and output
electrical signal is monitored by a Solatron 1260&1287 electrochemical workstation coupled with a 12V/20A power booster. The SOEC is heated and kept at a constant temperature of ~800°C by a furnace with integrated thermocouples. The outlet gas from the SOEC is directed into a dehumidifier, where the steam in the gas is removed. The volumetric flow rate ($Q_o$) and composition of the outlet gas is analysed by a volumetric flow meter and an Agilent 7820 gas chromatography. The utilization of steam ($U_s$) and CO$_2$ ($U_{CO2}$) is calculated according to equation (6-7) below:

$$U_s = \frac{(Q_o \cdot C_{H2,O} - Q_{H2,i})}{Q_{s,i}}$$ \hspace{1cm} (6)

$$U_{CO2} = \frac{Q_o \cdot C_{CO,O}}{Q_{CO2,i}}$$ \hspace{1cm} (7)

where, $C_{H2,O}$ is the H$_2$ content in the outlet gas while $C_{CO,O}$ is the CO content in the outlet gas.

The impedance curves of the button cell at different atmospheres is measured with the Solatron 1260 impedance analyser in the frequency range from 100 kHz to 0.1 Hz with the amplitude of 10 mV at open circuit. The ohmic resistance ($R_\Omega$) is measured from the high frequency intercept and the polarization resistance ($R_p$) is obtained from the differences between the high- and low-frequency intercepts on the impedance spectra. The $I$-$V$ curve is measured in the voltage range of 0-0.6V at a scan rate of 50 mV s$^{-1}$.

3. Results and Discussion

One significant advantage of HT steam/CO$_2$ coelectrolysis lies in the
flexibility of adjusting the outlet syngas composition by varying the operation conditions, such as the inlet gas composition and the electrolysis current density. Therefore, the effect of the inlet gas composition on the electrochemical performance, outlet syngas composition, and the steam/CO₂ utilization is investigated. Fig.3 shows the electrochemical performance of HT steam/CO₂ electrolysis with different inlet gas compositions at 800°C using button cells. In the figure, the inlet gas with a CO₂ concentration of ‘0’ corresponds to the atmosphere for HT steam electrolysis while the inlet gas with a CO₂ concentration of ‘80%’ corresponds to the atmosphere for HT CO₂ electrolysis. In different atmospheres with variant steam/CO₂ concentration ratio, the cell maintains nearly constant ($R_Ω$) values with minor difference at 800°C, illustrating the stable electrode/electrolyte contact condition and ionic conductivity of the electrolyte.

The polarization resistance ($R_p$) is 0.32, 0.35, 0.31, 0.44 and 0.86 Ω cm² for the cell when the CO₂ content in the inlet gas is 0, 20%, 40%, 60% and 80%, respectively. It indicates that the inlet gas composition has significant influence on the related reaction kinetics only when the CO₂ content is above 60%. It is also supported by the area specific resistance (ASR) derived from the slope of the $I-V$ curves in the electrolysis current density range of 0-0.6 A cm⁻² (Fig.3b). ASR for the cell in different atmospheres is 0.75, 0.78, 0.70, 0.79 and 1.06 Ω cm² when the CO₂ content in the inlet gas is 0, 20%, 40%, 60% and 80%, respectively. The results confirm the superior performance of HT steam electrolysis and steam/CO₂ coelectrolysis to the HT CO₂ electrolysis, in agreement with the report of Carl. M.
Stoots et al..

During the HT steam/CO$_2$ coelectrolysis process, two possible reactions, including the electrochemical reduction reaction of CO$_2$ (equation 2) and the RWGS chemical reaction (equation 3), may be responsible for the formation of CO. The $ASR$ value, which has no direct relationship with the kinetics of the RWGS reaction, has a strong dependence on the performance of the electrochemical reduction of CO$_2$ and steam. As a result, it can be used to evaluate the contribution of the electrochemical reduction reaction in the formation of CO during HT steam/CO$_2$ coelectrolysis considering the much slower kinetics of HT CO$_2$ electrolysis over HT steam electrolysis. An increased $ASR$ value should have been observed for HT steam/CO$_2$ coelectrolysis as the contribution of the electrochemical reduction reaction in CO formation increases. Nevertheless, similar $ASR$ values for HT steam/CO$_2$ coelectrolysis and HT steam electrolysis are achieved here, proving that most the CO is formed via the RWGS reaction rather than the electrochemical reduction reaction. Considering the close Gibbs free energies ($\Delta G$) for steam and CO$_2$ dissociation reaction at 800°C$^9$, the higher $ASR$ values for HT CO$_2$ electrolysis may be caused by the poorer intrinsic catalytic activity of Ni-YSZ towards the electrochemical reduction reaction of CO$_2$ or the slower diffusion kinetics of the CO$_2$ over steam inside the porous electrode. The results of Zhongliang Zhan et al. indicate that the calculated diffusion coefficient of steam at 800°C is $\sim 2.86$ cm$^2$ s$^{-1}$, two times that of 1.43 cm$^2$ s$^{-1}$ for CO$_2$ at the same temperature, consistent with the observed increase in the
low-frequency arc in the nyquist plots, associated with the gas diffusion process, as the CO₂ concentration in the inlet gas of H₂/H₂O/CO₂ for HT steam/CO₂ coelectrolysis increases. So the slower diffusion kinetics of CO₂ over steam comprises one important reason for the increased ASR value while the CO₂ concentration in the inlet gas during HT steam/CO₂ coelectrolysis increases. Nevertheless, influence of the intrinsic catalytic activity of Ni-YSZ towards different electrochemical reactions can still not be excluded because it is still unclear whether Ni-YSZ has similar intrinsic catalytic activities towards the electrochemical reduction reactions of steam and CO₂ at the high temperature. A detailed investigation will be conducted in the future to clarify this question.

Fig.4 shows the open circuit voltage (OCV) of the single cell in different atmospheres at 800°C. Fig.5 shows the syngas composition and the steam/CO₂ utilization of the cell operated at 800°C under a constant current density of 0.15 A cm⁻² after the removal of steam in the outlet gas. The single cell in pure hydrogen delivers a stable OCV value of ~1.10V during the test, indicating the good sealing effect. In the atmospheres for HT electrolysis, OCV is 0.89, 0.86, 0.88, 0.88 and 0.95 V when the CO₂ content in the inlet gas is 0, 20%, 40%, 60% and 80%, respectively. The slightly higher OCV value of 0.95V for HT CO₂ electrolysis at a CO₂ content of 80% is probably caused by the ~8% of CO formed via the RWGS reaction, as illustrated by the outlet syngas composition analysis in Fig.5a. The inlet gas composition does not have obvious influence on OCV, which can be explained in terms of the close Gibbs free energies for steam
and CO$_2$ splitting at 800°C$^{15}$.

At the open circuit condition, $\sim$1-8% of CO is formed via the RWGS reaction in the atmospheres for HT coelectrolysis, depending on the CO$_2$ content in the inlet gas. The increase in the CO$_2$ content in the inlet gas results in the shift of the RWGS equilibrium to the right side and thereby the increased concentration of CO produced via the RWGS reaction. Compared with the CO and H$_2$ content at OCV, a significant increase in the CO and H$_2$ content is observed when an electrolysis current density of 0.15 A cm$^{-2}$ is applied. For example, the H$_2$ content in the outlet gas increases from 15% at OCV to 30% at 0.15 A cm$^{-2}$ while the CO content increases from 3% to 17% correspondingly at the inlet gas composition of 20% H$_2$/40% steam/40% CO$_2$. It clearly demonstrates the effect of the input electric power on the outlet gas composition of the HT steam/CO$_2$ coelectrolysis system. However, a low steam/CO$_2$ utilization of $\sim$20-40% is obtained due to the low electrolysis current density of 0.15 A cm$^{-2}$ (Fig.5b). The H$_2$/CO content ratio in the outlet gas during HT steam/CO$_2$ coelectrolysis ranges from 6:1 to 1:1 with the inlet gas composition, confirming the feasibility of adjusting the syngas composition by controlling the inlet gas composition (Fig.5c). It should be noted that the 20% H$_2$ as the protection gas is also included in the outlet H$_2$ during the calculation process of the H$_2$/CO content ratio.

The outlet syngas composition and steam/CO$_2$ utilization are also measured at 800°C at different electrolysis current densities of 0-1.0 A cm$^{-2}$ with a fixed inlet gas composition of 20% H$_2$/40% steam/40% CO$_2$ and the corresponding results
are shown in Fig.6. In previous studies on HT steam/CO$_2$ coelectrolysis, a linear relationship in the whole current density range was observed in the plots of the CO, H$_2$ and CO$_2$ content in the outlet gas as a function of the current density $^8, 19$. Two linear regions, including region I with a larger slope between 0-0.4 A cm$^{-2}$ and region II with a lower slope between 0.4-1.0 A cm$^{-2}$, are clearly observed here, which may be ascribed to the different microstructure of the single cell and operation conditions adopted in the study. In region II, a slower increase in the H$_2$ and CO content appears as a function of the electrolysis current density, an obvious phenomenon of steam/CO$_2$ starvation at the cathode/electrolyte interface within the high current density region. It is also validated by the different ASR values calculated within the two regions. In region II, a much larger ASR of 1.35 $\Omega$ cm$^2$ is calculated compared to an ASR of 0.70 $\Omega$ cm$^2$ in region I (Fig.5d). Therefore, it is electrically more efficient to operate the HT coelectrolysis system at a current density below 0.4 A cm$^{-2}$ within region I. Additionally, it is also relevant to expand the maximum current density in region I by optimizing the microstructure of SOECs to facilitate the diffusion process of the reactant gas.

Both of the H$_2$ and CO content in the outlet gas increases significantly with the electrolysis current density. A maximum value of 41% and 37% for H$_2$ and CO is observed at the current density of 1.0 A cm$^{-2}$. Meanwhile, the steam utilization increases from -8.0% at OCV to 76% at 1.0 A cm$^{-2}$ and the CO$_2$ utilization increases from 13% to 77% accordingly. The negative steam utilization is attributed to the formation of CO through the RWGS reaction at the open circuit condition, which
consumes part of the 20% H\(_2\) in the inlet gas as the protection gas of the Ni-YSZ composite cathode. Similarly, the H\(_2\)/CO content ratio also varies obviously with the current density from 1.9 at OCV, to 1.5 at 0.1 A cm\(^2\), 1.2 at 0.4 A cm\(^2\) and 1.1 at 1.0 A cm\(^2\), indicating the high sensitivity of the outlet syngas composition to the electrolysis current density applied. During the synthesis of hydrocarbons or methanol from syngas via the catalytic processes, such as the Fisher-Tropsch process, the desired H\(_2\)/CO content ratio varies from \(~1.4\) to 2.1, which can be flexibly achieved by adjusting the operation conditions like the inlet gas composition or the electrolysis current density\(^\text{22, 23}\). It also comprises one important advantage of HT steam/CO\(_2\) coelectrolysis. Therefore, the inlet gas composition and electrolysis current density are two important parameters which should be fully considered in the operation.

4. Conclusions

The reaction characteristics of syngas production by HT steam/CO\(_2\) coelectrolysis with commercially available solid oxide electrolysis cells are systematically studied. During the inlet gas composition range (20% H\(_2\) / 20-80% CO\(_2\) / remaining steam) studied, the electrochemical performance of HT steam/CO\(_2\) coelectrolysis is close to that of HT steam electrolysis and much superior to that of HT CO\(_2\) electrolysis, supported by an ASR of 0.75 Ω cm\(^2\) for HT steam electrolysis, 0.70-0.79 Ω cm\(^2\) for HT coelectrolysis, and 1.06 Ω cm\(^2\) for HT CO\(_2\) electrolysis. It clearly indicates the important role of RWGS reaction in the formation of CO during the HT steam/CO\(_2\) coelectrolysis process. The outlet syngas composition after the removal of steam varies significantly with a H\(_2\)/CO
content ratio of 1.0-6.0 as a function of the CO$_2$ concentration in the inlet gas and a ratio of 1.9-1.0 as a function of electrolysis current densities, confirming the feasibility of controlling the syngas composition by adjusting the operation conditions. The electrolysis current density has a significant influence on the steam/CO$_2$ utilization with a maximum value of 76% for CO$_2$ and 77% for steam at a high current density of 1.0 A cm$^{-2}$.

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single column (8.3cm)
64x24mm (300 x 300 DPI)