A Novel Clean and Effective Syngas Production System Based on Partial Oxidation of Methane Assisted Solid Oxide Co-electrolysis Process

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Abstract

Development of the syngas production from solid oxide H₂O/CO₂ co-electrolysis is limited by the intensive energy input and low efficiency. Here, we present a new concept to efficiently generate syngas in both sides of the solid oxide electrolyzer by synergistically combining co-electrolysis with partial oxidation of methane (POM). Thermodynamic calculation and electrochemical measurements for the POM assisted solid oxide co-electrolysis processes on the SFM-SDC/LSGM/SFM-SDC cells exhibited an reduced electric input, increased energy conversion efficiency and decreased [cathodic co-electrolysis polarization resistance](#) in comparison with the conventional co-electrolysis. This method will be crucial to establish a clean and effective energy conversion system to meet global sustainable energy needs.

Keywords

Syngas production; Solid oxide co-electrolysis cell; Partial oxidation of methane; Efficiency

1. Introduction

Solid oxide co-electrolysis cell is a promising energy conversion device for splitting H_2O and CO_2 to produce syngas (mixture of H_2 and CO), which can be subsequently used as feedstock through the well-established Fischer-Tropsch (F-T) process to produce liquid synthetic fuel that can easily be stored and transported using the existing infrastructure compared with the alternative hydrogen[1, 2]. Compared to the traditional syngas production from coal gasification or steam reforming of natural gas, solid oxide co-electrolysis method doesn't consume fossil fuels and can electrochemically utilize CO_2 instead of emitting it[3, 4]. Although solid oxide co-electrolysis technique has great potential to solve the energy and environmental issues, there are still many challenges before it becomes practically feasible [5-8]. For the state-of-the-art solid oxide co-electrolysis cell system, the cathode is typically composed of Ni-based cermet material, which is easily oxidized losing its electrical and catalytic properties. Consequently, reducing gases such as H_2 and/or CO are required to feed together with the co-electrolysis reactant CO_2 and H_2O to maintain the reducing atmosphere in the cathode. Meanwhile, the anode is often directly exposed to air. The large oxygen partial pressure gradient across the electrolyte produces a high open circuit voltage (OCV) normally up to 1 V at the typical operating temperature, according to the Nernst equation. Since a voltage higher than the OCV must be supplied to the co-electrolysis cell in order to pump oxygen from the cathode side to the anode side during the co-electrolysis process, the majority of the electricity input is typically consumed to overcome the large oxygen potential gradient in the co-electrolysis process, resulting in a large amount of useless electricity consumption, and leading to substantially low electrolysis efficiency[9].

Reducing substances such as H_2 , CO , CH_4 and carbon have been reported to assist the steam splitting process for hydrogen production on the steam electrolyzer with a dramatically decreased electric input [9-12]. However, the amount of H_2 and CO produced via electrolysis reaction in the $\text{CO}_2/\text{H}_2\text{O}$ side is equivalent to the amount consumed in the H_2/CO feeding side when H_2 and CO are used to assist steam electrolysis, making it unpractical [10, 13]. It's also a huge waste and environmental unfriendly in case of

full oxidization of precious CH₄ fuel [12], which would be more attractive to yield valuable syngas H₂/CO by partial oxidation using oxygen as the oxidant [13-16]. The POM reaction ($\text{CH}_4 + 0.5\text{O}_2 = \text{CO} + 2\text{H}_2$) is mildly exothermic with a negative $\Delta H_{1173\text{K}}$ about -23.1 kJmol⁻¹, which can be used to compensate the energy demand of the co-electrolysis process. Meanwhile, the H₂/CO ratio of 2 from POM is an ideal feedstock for the downstream gas to liquid fuel production via existing processes such as F-T and methanol synthesis [17]. Although the overall reaction of the POM assisted co-electrolysis process is the same as that for methane H₂O/CO₂ reforming, it is more advantageous to perform the reforming by an electrical-to-chemical energy conversion route on a solid oxide cell, which is promising to serve as load lever and energy storage between electricity and fuel. In addition, POM assisted co-electrolysis can be implemented as distributed syngas generation units under atmospheric pressure compared to steam reforming which typically operates as large chemical plant in pressurized operation.

In this work, we present a novel strategy to achieve a significantly more efficient syngas production system by synergistically combining solid oxide co-electrolysis cell and partial oxidation of methane. Thermodynamic calculations are conducted to study the features of the POM assisted solid oxide co-electrolysis process. The feasibility of the POM assisted solid oxide co-electrolysis process are studied by the electrochemical measurements on the Sr₂Fe_{1.5}Mo_{0.5}O_{6- δ} (SFM)-Sm_{0.2}Ce_{0.8}O_{1.9} (SDC)/La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM)/SFM-SDC cells, which also perform the conventional co-electrolysis as a comparison.

2. Experimental

2.1. Preparation of electrodes, electrolyte powders

Sr₂Fe_{1.5}Mo_{0.5}O_{6- δ} (SFM) powders were synthesized by a glycine and citric acid assisted combustion method [18]. Sr(NO₃)₂, Fe(NO₃)₃·9H₂O and (NH₄)₆Mo₇O₂₄·4H₂O were used as metal precursors. Glycine and citric acid were used to assist the combustion process. The as-prepared ash was fired at 1050 °C for 5 h to form the perovskite structure. Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) powders were made by a glycine assisted combustion method [19]. The as-prepared powders were fired at 600 °C for 2 h to form the fluorite

structure. $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) electrolyte material was synthesized by the solid-state reaction [20].

2.2. Preparation of single cells

Dense LSGM electrolyte support was prepared by pressing LSGM powders into pellets and then sintering at 1450 °C for 5 hours. The electrode ink consisting of 60wt% SFM and 40 wt% SDC was screen printed on both sides of the LSGM electrolyte and then fired at 1050 °C for 2h. The effective electrode area was about 0.33 cm². Au paste was used as the current collector.

2.3. Cells Characterization

Schematic of the experimental apparatus for the high temperature co-electrolysis measurement was shown in Figure 1. The prepared SFM-SDC/LSGM/SFM-SDC single cell was firstly sealed onto an alumina tube using the conducting paste (DAD-87, Shanghai Research Institute of Synthetic Resins, China). High temperature ceramic adhesives (Ceramabond 552, Aremco) was then applied outside the sealed cells to further prevent leaking. The alumina tube with the well-sealed single cell was subsequently placed into a second larger quartz tube with one end closed. The two tubes setup allowed the gas conditions fed to both the electrode compartments exactly determined. The amount of CO₂, H₂ and N₂ were controlled by mass flow controllers (APEX, Alicat Scientific, U.S.). The steam vapor with specific water partial pressure was generated using a humidifier by heating the liquid water to a certain temperature [21]. Heating tapes are used to wrap the gas pipes to avoid condensation. The exact water partial pressure of the inlet gases was continuously measured using a humidity sensor (Vaisala, HMP 337). Electrochemical characterizations including current density-voltage (i-V) and impedance spectra measurements for the single cells were conducted on a Versa STAT 3-400 test system (Princeton Applied Research). The i-V curves were recorded from OCV to OCV+0.5V with a sweeping speed of 0.03 Vs⁻¹. Electrochemical impedance spectra (EIS) under both OCV and electrolysis conditions were measured with the amplitude of 10 mV and then fitted using the Z-view software. Thermodynamic calculation as function of temperature were conducted using the HSC software (version 5.0).

3. Results and discussions

Figure 2 illustrates the working principle for the POM assisted solid oxide co-electrolysis cell in comparison with the conventional co-electrolysis. A feed stream consisting of H_2O and CO_2 is introduced to the cathode, where H_2O and CO_2 accept electrons from an external circuit to produce H_2 , CO and oxygen ions, O^{2-} , as described in [Eq. (1)] and [Eq. (2)],

Different from the conventional co-electrolysis process (as shown in Figure 2a), a stream of CH_4 is fed to the anode to react with oxygen ions supplied from the electrolyte in the POM assisted mode (as shown in Figure 2b). Consequently, CO and H_2 are expected to form in the anode by the partial oxidation of methane, as described in [Eq. (3)].

The overall reaction for solid oxide co-electrolysis cell operated in the conventional and POM assisted modes can be written in [Eq. (4)] and [Eq. (5)], respectively,

There are several profound advantages for the POM assisted co-electrolysis process. First of all, syngas with favorable H_2/CO ratio for downstream chemical synthesis can be achieved in both electrode sides of the solid oxide cell by adjusting H_2O/CO_2 and CH_4/O^{2-} (current density) ratio [1, 22]. Second, supplying methane in the anode compartment can substantially lower the OCV of the co-electrolysis cell, leading to significantly lower electrical energy demand for the electrolysis reaction. Third, heat released from the exothermic POM reaction can be used by the endothermic electrolysis process; oxygen produced from the co-electrolysis process can be directly utilized by the POM reaction on the electrolyzer. Furthermore, the

partial oxidation of methane can also improve the co-electrolysis conversion rate, since one of the co-electrolysis products, O^{2-} , is constantly consumed by reacting with methane.

Thermodynamic calculations are conducted to study the features of the POM assisted solid oxide co-electrolysis process. When the co-electrolysis process is performed in the conventional mode as described by [Eq. (4)], the total required energy ΔH is 528 kJmol^{-1} , insensitive to temperature from 200 to 1000°C , as shown in Figure 3a. Although electric energy demand ΔG decreases with the temperature and the corresponding increase in heat energy Q due to positive entropy change, ΔS of the co-electrolysis reaction, ΔG still maintains a high positive value above 300 kJmol^{-1} even at 1000°C . This relatively high electric energy demand definitely restricts the competitiveness of the conventional solid oxide co-electrolysis process, since electricity is typically more expensive than heat. However, when the co-electrolysis process is performed by the POM assisted mode as described in [Eq. (5)], the total energy ΔH has decreased 9% from the previous 528 to 481 kJmol^{-1} as shown in Figure 3b, indicating a reduction in energy input for the proposed novel co-electrolysis mode as a result of some portion of the endothermic co-electrolysis process being compensated by heat released from the exothermic POM reaction. Most noticeably, for POM assisted co-electrolysis mode as shown in [Eq. (5)], the electrical energy demand ΔG exhibits a negative value at around 650°C and the Gibbs free energy change ΔG becomes more negative with increasing the temperature, indicating that POM assisted co-electrolysis process can occur spontaneously without the input of external electricity when the operating temperature is above 650°C . This is extremely significant considering that heat input can be supplied from industrial waste heat, or from concentrated solar panel.

To evaluate the feasibility of POM assisted co-electrolysis technique, symmetrical cells, SFM-SDC/LSGM/SFM-SDC, that can work in both conventional and POM assisted modes are investigated to exclude the influence of material composition and microstructure of the cell components from different cells. SFM is chosen for the excellent reduction/oxidation (redox) stability and good electrical properties in a broad range of oxygen partial pressure [23]. SDC is incorporated to increase the electrode ionic

conductivity, and consequently improve the cell performance due to enlarged active reaction sites [24, 25]. As shown in Figure 4, the i - V curve for the POM assisted mode is far below the conventional one, indicating that a much lower voltage is required to produce the same amount of electrolysis current. For instance, at 800 °C, the potential to produce electrolysis current of 200 mAcm⁻² is 1.13 V for the conventional co-electrolysis with the anode exposed to air; while the potential has decreased by nearly one order of magnitude to 0.14 V when the cell is operated under POM assisted mode in which partial oxidation of methane takes place in the anode. Another evidence for the enhancement is from the OCV of the co-electrolysis process. The cell OCV for the POM assisted co-electrolysis has dropped from a normally high positive 0.89 V of the conventional co-electrolysis process to a negative -0.19 V, consistent with the negative ΔG at 800 °C according to the above thermodynamic analysis. The remarkable decrease in the OCV demonstrates that the energy barrier for the electrolysis reaction is much lower in the POM assisted co-electrolysis mode than the conventional co-electrolysis process. The negative OCV also suggests that co-electrolysis occurs spontaneously with the assistance of partial oxidation of methane in the anode side. This will significantly improve the economic competitiveness of the solid oxide co-electrolysis process, which has not been applied in large-scale application mainly due to substantial electricity cost. In particular, the introduction of methane in the anode has resulted in a quite unique behavior within the potential range from -0.19 to 0 V. On one hand, the positive power density indicates that the SFM-SDC/LSGM/SFM-SDC cell generates electricity as does in a solid oxide fuel cell. On the other hand, the positive over-potential compared with OCV indicates that the cathode is consuming electrons to perform CO₂/H₂O electrolysis. At the same time, syngas of CO and H₂ is produced in both electrodes. Both current flow and syngas generation are driven by the oxygen chemical potential difference between the two electrodes without external electric energy input. The current corresponding to the syngas production continues to increase with the applied potential, and an electrolysis current of 350 mAcm⁻² can be obtained at a cell voltage of only 0.4 V in the POM assisted mode.

Although it has been demonstrated that the electric consumption can be substantially reduced by the introduction of methane, the POM assisted co-electrolysis process may lead to useful energy loss since

some portion of chemical energy from methane is converted into heat instead of electricity or chemical energy stored in syngas. Therefore, it is necessary to evaluate the energy efficiency defined as how much energy converted to the desirable product [26]. Assuming that the products H_2 and CO are formed only through the electrolysis process, and the high temperature H_2O/CO_2 co-electrolysis process on the solid oxide SDC-SFM/LSGM/SDC-SFM cell occurs as described in [Eq. (4)], the current consumed to produce H_2 by splitting H_2O will be the same as that consumed to produce CO by splitting CO_2 . The electricity input Q_{ele} ($kJ s^{-1}$) can be written as

$$Q_{ele} = 10^{-3} \times IV \quad (6)$$

Where I (A) is the electrolysis current, and V (V) is the applied voltage.

The mole rate of H_2 and CO production, N_{H_2} ($mol s^{-1}$) and N_{CO} ($mol s^{-1}$) by splitting H_2O and CO_2 , can be determined using the Faraday's law

$$N_{H_2} = N_{CO} = 0.5 \times \frac{I}{2F} \quad (7)$$

The reversible heat, Q_{re} ($kJ s^{-1}$), for the conventional solid oxide co-electrolysis process is related to the working temperature T (K), the entropy change ΔS ($JK^{-1}mol^{-1}$) and the reacted mole rate.

$$Q_{re} = 10^{-3} \times \frac{I}{4F} T \Delta S \quad (8)$$

The irreversible heat, Q_{ir} ($kJ s^{-1}$), is the released energy resulted from the polarization resistance of the cell, and can be expressed as

$$Q_{ir} = 10^{-3} \times I(V - V_{ocv}) \quad (9)$$

The heat required for heating the reactants, H_2O and CO_2 , from T_0 to the operating temperature T is determined by

$$Q_{H_2O} = \frac{F_{H_2O}}{22.4 \times 1000 \times 60} \times 10^{-3} \times \int_{T_0}^T C_{P,H_2O} dT \quad (10)$$

$$Q_{CO_2} = \frac{F_{CO_2}}{22.4 \times 1000 \times 60} \times 10^{-3} \times \int_{T_0}^T C_{P,CO_2} dT \quad (11)$$

Where F_{H_2O} (sccm) and F_{CO_2} (sccm) are the mass flow of H_2O and CO_2 .

In the conventional co-electrolysis process, H_2 and CO are produced from heat and electricity input while some amount of heat is released due to cell polarization. Since the irreversible heat, Q_{ir} , is always less than the reversible heat, Q_{re} , in the entire range of the current density between 0 to -350 mAcm^{-2} , only efficiency in the case of $Q_{ir} < Q_{re}$ is considered which can be calculated using [Eq. (12)]

$$\eta = \frac{N_{H_2} LHV_{H_2} + N_{CO} LHV_{CO}}{Q_{ele} + (Q_{re} - Q_{ir}) + Q_{CO_2} + Q_{H_2O}} \quad (12)$$

Where LHV_{H_2} and LHV_{CO} are the lower heating value of H_2 and CO , respectively. All the parameters used in the energy efficiency calculation for the conventional co-electrolysis process can be found in Table 1.

As shown in Figure 4, the efficiency for the conventional co-electrolysis process on the SFM-SDC/LSGM/SFM-SDC cell increases with the current density. The trend is consistent with that reported in solid oxide steam electrolysis cells [28]. For POM assisted co-electrolysis process, when $V_{OCV} < V \leq 0$ & $Q_{re} > Q_{ir}$, syngas and electricity are co-generated with the corresponding efficiency shown as [Eq. (13)]

$$\eta = \frac{Q_{ele} + N_{H_2} LHV_{H_2} + N_{CO} LHV_{CO}}{N_{CH_4} LHV_{CH_4} + (Q_{re} - Q_{ir}) + Q_{CO_2} + Q_{H_2O} + Q_{CH_4}} \quad (13)$$

However, when $V > 0$, the case becomes similar to the conventional co-electrolysis process except for additional energy input from CH_4 .

$$\eta = \frac{N_{H_2} LHV_{H_2} + N_{CO} LHV_{CO}}{N_{CH_4} LHV_{CH_4} + Q_{ele} + (Q_{re} - Q_{ir}) + Q_{CO_2} + Q_{H_2O} + Q_{CH_4}} \quad (14)$$

Where N_{CH_4} is the mole rate of the reacted CH_4 , LHV_{CH_4} is the lower heating value of CH_4 , and Q_{CH_4} is the heat required for heating up the CH_4 . The efficiency for the POM assisted co-electrolysis on the same SFM-SDC/LSGM/SFM-SDC cell in Figure 4 also increases with the current density. However, the efficiency value for POM assisted co-electrolysis mode is obviously higher than that of the conventional mode. For example, the data at 200 mAcm^{-2} is 0.33, about 57% higher than 0.21 for the conventional mode. Therefore, both the reduced electric input and the increased energy conversion efficiency have confirmed the promotion effect of the co-electrolysis process with the assistance of partial oxidation of methane.

Electrochemical impedance spectra are measured in three different conditions for the SFM-SDC/LSGM/SFM-SDC cell in both the conventional and POM assisted co-electrolysis modes. EIS data are recorded from 1 MHz to 0.1~0.01 Hz with an amplitude of 10 mV and then fitted using the Z-view software with the equivalent circuit $R_0(\text{RiCPEi})$, where R_0 is related to the overall ohmic resistance from the electrolyte, electrodes and the lead wires, while (RiCPEi) represents a depressed semi-circle in the Nyquist plot and a symmetrical peak in the Bode plot that is related to the i^{th} specific sub-step of the overall electrochemical reaction. The equivalent capacitance C and typical frequency f , which is independent of sample geometric characteristic and is a very useful tool to identify the electrochemical process, are also calculated based on the following equation [29]:

$$C_i = \frac{(R_i Q_i)^{1/n_i}}{R_i} \quad (15)$$

$$f_i = \frac{(R_i Q_i)^{-1/n_i}}{2\pi} \quad (16)$$

The ohmic resistance R_0 at 800°C in the conventional mode is $0.26 \text{ }\Omega\text{cm}^2$, which is slightly larger than $0.20 \text{ }\Omega\text{cm}^2$ in the POM assisted mode. This is possibly attributed to the conductivity difference of electrolyte and/or electrode material in the reducing and oxidizing atmosphere. It has been reported that the conductivity of LSGM is almost independent of oxygen partial pressure in region of $10^{-22} \sim 1 \text{ atm}$ [20].

However, the SFM material has a higher conductivity in the reducing atmosphere than that in the oxidizing atmosphere, presenting 32 Scm^{-1} in wet H_2 and 14.9 Scm^{-1} at 750°C in air, respectively [24, 25]. The feature of electrical property has also been observed in other double-perovskites Sr_2MMoO_6 ($\text{M}=\text{Co}, \text{Ni}$), which show the highest conductivity in methane, then in hydrogen and lowest in air [30]. The electrode reaction process is also quite different in the two modes. When the cell is operated in the conventional mode, only one obvious arc is present in the Nyquist plot measured under OCV as shown in Figure 5a. At the same time, the corresponding Bode plot shows only one symmetrical peak in Figure 5b. The reaction step has an equivalent capacitance $\sim 0.01 \text{ Fcm}^{-2}$, a typical frequency $\sim 11 \text{ Hz}$, and a polarization resistance about $1.19 \text{ }\Omega\text{cm}^2$. However, when the cell is operated in the POM assisted mode, an additional arc (R2CPE2) is present besides the first arc at a distinguishably lower frequency in the impedance spectra measured under OCV. Meanwhile, in the Bode plot it shows an overlap of two different peaks at the frequency of ~ 10 and $\sim 0.1 \text{ Hz}$. According to the fitting results in Table 2, the high frequency sub-step has an equivalent capacitance $\sim 0.04 \text{ Fcm}^{-2}$, a typical frequency $\sim 4 \text{ Hz}$, and a polarization resistance about $0.99 \text{ }\Omega\text{cm}^2$. Since the first arc in the POM assisted mode shows similar order of frequency to those measured in the conventional co-electrolysis process, the characteristics in the typical frequency demonstrates that the reaction step corresponding to the first arc is similar in the conventional and POM assisted co-electrolysis modes. Consequently, the high frequency arc may be related to the cathodic co-electrolysis process occurred in both modes. However, it should be noted that the reaction rate of the sub-step has been accelerated in the POM assisted mode with a reduced resistance of $0.99 \text{ }\Omega\text{cm}^2$, compared to $1.19 \text{ }\Omega\text{cm}^2$ in the conventional mode, since one of the co-electrolysis reaction products in the cathode, O^{2-} , is timely consumed by reacting with methane in the anode. This second

reaction step in the POM assisted mode has totally different characteristics with a larger equivalent capacity $\sim 3.66 \text{ Fcm}^{-2}$ and a lower typical frequency $\sim 0.07 \text{ Hz}$, which is potentially caused by the introduction of methane in the anode. The additional low frequency sub-step has a polarization resistance of $0.6 \Omega\text{cm}^2$, contributing to a higher total electrode polarization resistance of $\sim 1.59 \Omega\text{cm}^2$ compared to $1.19 \Omega\text{cm}^2$ in the conventional mode. Impedance spectra under the POM assisted mode are also recorded at a higher applied potential, $OCV+0.3V$. As we mentioned above that all the oxygen ions consumed in the POM reaction are supplied by the co-electrolysis process, a more intensive enhancement is expected to occur at a higher applied voltage to generate more oxygen ions. From the fitting results shown in Table 2, both high and low frequency polarization resistance $R1$ and $R2$ measured under a potential of $OCV+0.3V$ in the POM mode decrease as expected, compared with that measured under the OCV condition in the POM assisted mode. Therefore, it can be concluded that the high frequency sub-step possibly related to cathodic co-electrolysis process has been promoted by the introduction of methane. The total electrode process could be accelerated at an increased applied voltage.

4. Conclusion

In summary, we have presented a new strategy for establishing a low-cost and effective syngas production system by combining high temperature co-electrolysis and partial oxidation of methane processes on the solid oxide electrolyzer. The electric energy input has been significantly decreased and the overall efficiency accordingly improved for the POM assisted co-electrolysis. Testing on symmetrical cells with the cell configuration of SFM-SDC/LSGM/SFM-SDC has validated the dramatic promotion by partial oxidation of methane for the co-electrolysis process with remarkably decreased voltage and cathodic co-electrolysis process.

Acknowledgements

This material is based upon work supported as part of the HeteroFoaM Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001061.

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Table captions:

Table 1. Parameters used in the energy efficiency calculation for the conventional and POM assisted co-electrolysis process

Table 2. Fitting results of the impedance spectra in Figure 5.

Table 1 Parameters used in the energy efficiency calculation for the conventional and POM assisted co-electrolysis process

Parameter	Value
H ₂ lower heating value, LHV_{H_2} , (kJmol ⁻¹) ^[12]	248.3
CO lower heating value, LHV_{CO} , (kJmol ⁻¹) ^[12]	282.4
CH ₄ lower heating value, LHV_{CH_4} , (kJmol ⁻¹) ^[12]	200.2
Initial temperature, T_0 , (K)	298
Operating temperature, T , (K)	1073
Faraday constant, F , (Cmol ⁻¹)	96485
H ₂ O mass flow rate, F_{H_2O} , (sccm)	7.5
CO ₂ mass flow rate, F_{CO_2} , (sccm)	8
CH ₄ mass flow rate, F_{CH_4} , (sccm)	20
H ₂ O heat capacitance, C_{p, H_2O} , (Jmol ⁻¹ K ⁻¹) ^[27]	$30.00+10.700\times 10^{-3}T-2.022\times 10^{-6}T^2$
CO ₂ heat capacity, C_{p, CO_2} , (Jmol ⁻¹ K ⁻¹) ^[27]	$26.75+42.258\times 10^{-3}T-14.25\times 10^{-6}T^2$
CH ₄ heat capacity, C_{p, CH_4} , (Jmol ⁻¹ K ⁻¹) ^[27]	$14.15+75.496\times 10^{-3}T-17.99\times 10^{-6}T^2$

Table 2. Fitting results of the impedance spectra in Figure 5.

	Conventional 800 °C, OCV	POM 800 °C, OCV	POM 800 °C, OCV+0.3V
R0(Ωcm^2)	0.26	0.20	0.20
R1(Ωcm^2)	1.19	0.99	0.86
Q1($\text{Scm}^{-2}\text{s}^n$)	0.089	0.19	0.17
n1	0.53	0.52	0.51
C1(Fcm^{-2})	0.012	0.040	0.028
f1(Hz)	10.94	4.05	6.67
R2(Ωcm^2)	---	0.60	0.40
Q2($\text{Scm}^{-2}\text{s}^n$)	---	3.46	1.89
n2	---	0.93	0.91
C2(Fcm^{-2})	---	3.66	1.84
f2(Hz)	---	0.072	0.21
Chi-Squared	0.0003	0.0003	0.0004

Figures captions:

Figure 1. Schematic of the experimental apparatus for the high temperature co-electrolysis measurement.

Figure 2. Working principle of a solid oxide co-electrolysis cell operated in a) conventional mode, and b) POM assisted mode.

Figure 3. Thermodynamic calculation as function of temperature for co-electrolysis process in a) conventional mode, and b) POM assisted mode.

Figure 4. i-V and i-efficiency curves for the SFM-SDC/LSGM/SFM-SDC cell operated in both conventional and POM assisted co-electrolysis modes. The gas fed to the cathode is consisted of $P_w=2.2$ psi, $F_{N_2}=24\text{sccm}$; $F_{CO_2}=8\text{sccm}$; $F_{H_2}=10\text{sccm}$; the gas fed to the anode is consisted of and $P_w=0.4$ psi, $F_{N_2}=30\text{sccm}$; $F_{CH_4}=20\text{sccm}$ for the POM assisted mode and $F_{Air}=50\text{sccm}$ for the conventional mode.

Figure 5. Impedance spectra in forms of a) Nyquist and b) Bode plots for SFM-SDC/LSGM/SFM-SDC cell operated in three different conditions.

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