Efficient syngas generation for electricity storage through carbon gasification assisted solid oxide co-electrolysis

Libin Lei ^a, Yao Wang ^{a,b}, Shumin Fang ^a, Cong Ren ^a, Tong Liu ^{a,b}, Fanglin Chen ^{a,*}

^a Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29208, USA

^b Department of Water Quality Engineering, School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, P. R. China

* Phone: +1 803 777 4875; Email: chenfa@cec.sc.edu

Abstract:

High temperature CO₂ and H₂O co-electrolysis is a promising way to produce syngas for the storage of electrical energy harvested from renewable energy sources. However, a significant portion of electricity input is consumed to overcome a large oxygen potential gradient between the electrodes in conventional solid oxide electrolysis cells (SOECs). In this study, we present a novel and efficient syngas generator integrating carbon gasification and solid oxide co-electrolysis to improve the system efficiency. The feasibility of this new system is demonstrated in La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) electrolyte-supported SOECs. Both thermodynamic calculation and experimental results show that the potential barrier for co-electrolysis can be reduced by about 1 V and the electricity input can be saved by more than 90% upon integration of SOECs with carbon gasification. On the anode side, “CO shuttle” between the electrochemical reaction sites and solid carbon is realized through the Boudouard reaction (C+CO₂=2CO). Simultaneous production of CO on the anode side and CO/H₂ on the cathode side generates syngas that can serve as fuel for power generation or feedstock for chemical plants. The integration of carbon gasification and SOECs

provides a potential pathway for efficient utilization of electricity, coal/biomass, and CO₂ to store electrical energy, produce clean fuel, and achieve a carbon neutral sustainable energy supply.

Keywords: Solid oxide electrolysis cell, carbon gasification, syngas production

1. Introduction

Fossil fuels, such as coal, oil and natural gas, are non-renewable energy resources and their ever-increasing consumption leads to excessive emission of greenhouse gases such as CO₂. Therefore, carbon emission reduction needs to be implemented and renewable energy sources have actively been developed globally in the past decades. Renewable energy sources such as wind and solar are now increasingly harvested to generate electricity, but the intermittent nature of these energy sources requires the capacity for large-scale electrical energy storage. Therefore, it's essential to develop efficient electricity storage technologies. Co-electrolysis of steam and carbon dioxide by solid oxide electrolysis cells (SOECs) is a promising energy storage method that can efficiently transform electrical energy into non-fossil syngas (a mixture of H₂ and CO) which can be converted to electricity when required[1-3]. Meanwhile, it is an excellent alternative for CO₂ utilization due to its high conversion rate and flexibility[4, 5]. The produced syngas can also be subsequently used as feedstock through the well-established Fischer-Tropsch (F-T) process to produce liquid synthetic fuel that can be easily stored and transported using the existing infrastructure compared with the alternative hydrogen[6].

However, there are still paramount challenges for the large scale deployment of SOECs[7-10]. One major challenge is that a significant portion of electricity input is

consumed to overcome a large oxygen potential gradient (open circuit voltage up to 1 V) in the co-electrolysis process, because the anode is often exposed to air with a high oxygen partial pressure[11]. Considering that the electrical consumption is crucial for its commercial competitiveness, it is very desirable to reduce the oxygen partial pressure of the anode in order to lower the open circuit voltage (OCV). Furthermore, utilization of oxygen produced in the anode is also vital for improving the overall system efficiency. However, there are only very limited reports concerning the reduction of oxygen potential gradient in SOECs. Martinez-Frias et al. reported that natural gas assistance can reduce the OCV of electrolysis and improve the efficiency with heat recovery system[11]. Wang et al. reported that introduction of reducing gases (CH_4 or CO) in the anode can decrease the electrochemical potential required for electrolysis [12, 13]. However in these studies, the utilization of oxygen produced in the anode is ignored. In contrast, We have recently demonstrated a strategy that combines partial oxidation of methane and co-electrolysis, in which the potential barrier is reduced and oxygen (produced in the anode) is used to partially oxidize methane to produce syngas[14].

Carbon gasification (CG) is a process to transform carbon-containing solids (such as coal and biomass) into gaseous fuels such as CO , H_2 , and CH_4 . It has emerged as a clean and effective way for the production of gaseous fuels that can be used for power generation or synthesis of chemicals [15, 16]. CG is already a well-developed technology and has been widely applied in Integrated Gasification Combined Cycle (IGCC), production of syngas, and solid oxide fuel cells (SOFCs) [17-29]. Similarly, solid oxide co-electrolysis and CG process can be synergistically combined and an integrated paradigm can be achieved. The

1 production of CO by carbon gasification in the anode side can eliminate the uphill potential
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3 barrier in SOECs. Furthermore, partial oxidation of carbon in the anode is an exothermic
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5 reaction that can provide heat for the endothermic electrolysis reaction in the cathode.
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7 Carbon-based solid oxide steam electrolysis, containing molten silver as the anode has been
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9 described theoretically [30]. Noticeably, above certain temperature, carbon-based solid
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11 oxide steam electrolysis process can occur spontaneously without input of external
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13 electricity. The feasibility of steam-carbon solid oxide electrochemical cells for hydrogen
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15 production has been reported [31-33]. However, the feasibility of syngas production has not
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17 been reported yet for carbon assisted SOECs. Compared with the steam electrolysis
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19 (hydrogen production), co-electrolysis of H₂O and CO₂ (syngas production) is not only an
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21 energy conversion method but also an effective CO₂ utilization method. Moreover, the
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23 behaviour of the CG process and the product in the anode side in CG-assisted SOEC have
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25 not been reported, which are critical to assess the energy efficiency of the system.
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36 In this work, we present a novel and efficient syngas generator, in which carbon
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38 gasification and solid oxide co-electrolysis process are synergistically combined, as schematically
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40 illustrated in Fig.1. The feasibility of this novel integrated system has been studied in
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42 La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) electrolyte-supported SOECs. The carbon gasification process in
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44 the anode side is investigated by thermogravimetry (TG) and gas chromatography (GC). Based on
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46 the electrochemical and GC data, electricity consumption and energy efficiency of this device are
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48 calculated to demonstrate its advantages.
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2. Experimental

2.1 The characterization of carbon powders

The carbon source used in this study is activated carbon with 10 wt.% Fe loading [25]. The gasification behaviours of carbon powder were studied by thermogravimetric analysis (STA 449 F1 Jupiter, Netzsch, Germany) in air and in CO₂ atmosphere, respectively over the temperature range of 323–1273 K. The heating rate was fixed at 5 K min⁻¹. The total flow rate of gases was 60 ml min⁻¹. Thermodynamic calculation was conducted using the HSC 6.0 software.

2.2 Preparation of single cells

Dense electrolyte support was prepared by pressing La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) (Fuel Cell Materials, USA) powders into pellets and then sintering at 1723 K for 5 h. After sintering, the LSGM pellet is 10.7 mm in diameter and 0.5 mm in thickness. The electrode ink consisting of 60 wt.% Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ} (SFM) and 40 wt.% Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) was screen-printed on both sides of the LSGM electrolyte and then fired at 1373 K for 2 h. The effective electrode area was about 0.33 cm². Gold paste was used as the current collector.

2.3 Cells characterization

A schematic of the experimental apparatus for the CG assisted co-electrolysis measurement is shown in Figure S1. The prepared SFM-SDC/LSGM/SFM-SDC single cells were sealed between two alumina tubes using silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins, China). High temperature ceramic adhesive (552-1105, Aremco, USA) was then applied outside the sealed cell to minimize gas leaking. 8 ml min⁻¹ CO₂ (16 vol.%), 10 ml min⁻¹ H₂ (20 vol.%), 24 ml min⁻¹ N₂ (48 vol.%) and 8 ml min⁻¹ H₂O

(16 vol.% AH) were introduced in the cathode side during the electrolysis test. The flow rates of CO₂, H₂ and N₂ were controlled by mass flow controllers (APEX, Schoonover, USA). Steam was generated using a humidifier by heating liquid water to a pre-determined temperature. Heating tape was used to surround gas pipes to avoid condensation. The exact water partial pressure of the inlet gases was continuously measured using a humidity sensor (HMP 337, Vaisala, USA). Carbon source was placed into the upper tube of the anode side. The exhaust gas with 5 mL min⁻¹ N₂ as sweep gas from the anode side was analysed by a gas chromatograph (7890A, Agilent, USA). Electrochemical characterizations including current density-voltage (*I-V*) and impedance spectra measurements for the single cells were conducted on an electrochemical test system (Versa STAT 3-400, Princeton Applied Research, USA). The *I-V* curves were recorded from OCV to OCV+1V with a voltage sweeping speed of 0.03 V s⁻¹. Electrochemical impedance spectra (EIS) under both OCV and electrolysis conditions (0.15 mA cm⁻²) were recorded with a voltage amplitude of 30 mV.

3. Results and discussion

3.1 The principle and thermodynamic calculation of conventional and CG assisted co-electrolysis

Fig.1 illustrates the working principle of the CG assisted co-electrolysis, which is the same as the conventional co-electrolysis in the cathode side. In both modes, a feed stream consisting of H₂O and CO₂ is introduced to the cathode, where H₂O and CO₂ accept electrons from an external circuit to produce H₂ and CO and oxygen ion O²⁻, as described in reactions (1) and (2). Reverse water gas shift reaction (RWGSR) also takes place in the cathode side, as described in reaction (3).

Compared with the conventional co-electrolysis, the significant distinction of the CG assisted co-electrolysis is that carbon source is introduced in the anode side, as shown in Fig.1 (within the dotted rectangle). Through the Boudouard reaction (reaction (4)), carbon reacts with CO_2 to produce CO. The produced CO diffuses to the triple phase boundary (TPB) sites of the anode to react with O^{2-} to form CO_2 , releasing electrons at the same time, as described in reaction (5). Consequently, a sustainable cycle is realized due to the diffusion of CO gases and the related reactions (4)-(5), similar to the “CO shuttle mechanism” in direct carbon solid oxide fuel cells (DC-SOFCs) [27].

The overall reaction of the CG assisted co-electrolysis is shown in reaction (6):

Fig.2 shows the thermodynamic calculation results for the co-electrolysis in different modes. When operated in the conventional mode, the process requires a total amount of energy (ΔH) about 528 kJ mol^{-1} in the temperature range from 400 to 1300 K. Although the electrical energy demand shown in Fig. 2(a) decreases at higher temperature with the significantly increase of heat due to the positive entropy change (ΔS), even at 1300 K, the ΔG still maintains at a high positive value above 300 kJmol^{-1} . Since electricity is much more valuable than joule heat which may be readily available in the typical industrial processes or

1 from solar heating, this inevitable high electrical input definitely degrades the
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3 competitiveness of the conventional solid oxide co-electrolysis technique.
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6 When the co-electrolysis process is performed in the CG assisted mode as described in
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8 reaction (6), the total energy decreases 41% from the conventional mode of 528 to 310
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10 kJmol^{-1} . Moreover, it is noticeable that the electrical energy demand ΔG reduces
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12 dramatically with temperature. When the temperature reaches 1000 K, the ΔG becomes a
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14 negative value, suggesting that the CG assisted co-electrolysis reaction can occur
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16 spontaneously without any external electrical input.
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22 Furthermore, compared with the conventional mode, operational voltage window of the
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24 system is much broader in the CG assisted mode, because the gap between thermal neutral
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26 voltage (E_{tn}) and reversible voltage (E_{re}) is larger in the CG assisted mode. Larger gap
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28 between E_{tn} and E_{re} makes electrolysis more flexible and efficient. The detailed calculation
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30 of the thermal neutral voltage E_{tn} and the reversible voltage E_{re} in different modes is
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32 included in the support information and the result is shown in Fig. S2.
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39 In thermodynamic term, the CG-assisted electrolysis reaction is identical to carbon gasification
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41 using steam and CO_2 as gasifying agents. However, there are several unique merits when it is
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43 performed in SOECs. The key point is that it is an electrical energy to chemical energy conversion
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45 on a solid oxide cell, which can also be directly used to generate electricity when operating in fuel
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47 cell mode. Thus the solid oxide cell can serve as load levelling and energy storage between
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49 electricity and fuel. Moreover, in the CG assisted electrolysis cell, the reaction and conversion rate
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51 of the gasification reaction can be controlled and managed by the applied current density. In
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53 addition, the design of the CG assisted electrolysis cell is flexible. It can be implemented as
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distributed syngas generation device under atmospheric pressure, while carbon gasification generally operates as large chemical plants in pressurized operation. The CG assisted electrolysis cell can also be implemented in large scale chemical plants or coal-based power plants. Lastly, because of the separation of carbon and gas agent in the CG assisted electrolysis cell, clean and pure syngas without contaminants such as H_2S and N_xO_y can be produced in the cathode so that dirty fuels such as coal can be potentially converted to green and clean fuels.

3.2 Electrochemical test of the conventional and the CG assisted co-electrolysis

To evaluate the feasibility of CG assisted co-electrolysis technique, symmetrical cells, SFM-SDC/LSGM/SFM-SDC, that can work in both the conventional mode and the CG assisted mode are fabricated and investigated to exclude the influence of material composition and microstructure of cell components from different cells. SFM is chosen for its good electrical properties and excellent redox stability [34]. It has been used as symmetrical electrode material in SOFC mode and SOE mode [35-37]. SDC is incorporated to increase the electrode ionic conductivity, and consequently improve the cell performance due to enlarged active reaction sites [38, 39]. Shown in Fig.3 (a) is the cross section microstructure image of the electrolysis cell, with symmetrical tri-layers structure. The LSGM electrolyte support layer, after sintered at 1723 K for 5h, is relatively dense. Fig.3 (b) displays that the porous SDC-SFM electrode is well adhered to the electrolyte after sintering at 1373 K for 2 h.

The I - V curves of the CG assisted mode and the conventional mode are shown in Fig.4 (a). It can be seen that at 1123 K, the OCV of the CG-assisted mode is -0.202 V, indicating that electrolysis in the CG-assisted mode is spontaneous (i.e., it is generating electricity),

1 while the voltage needed for the electrolysis process of the conventional mode is 0.877 V. It
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3 is noted that in order to enhance the electrode kinetics and have relatively high electrolysis
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5 current density in practical applications, an external electricity input is needed for the CG
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7 assisted mode even at an operating temperature higher than 1123K. However, it can be seen
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9 that the I-V curve measured under the CG assisted mode totally stays below the one
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11 measured under the conventional mode, indicating that a much lower voltage is required to
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13 produce the same electrolysis current density. For example, the cell voltage to produce
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15 electrolysis current density of 0.4 A cm^{-2} is 0.9 V for the conventional mode; while the
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17 required voltage has been decreased dramatically by nearly one order of magnitude to 0.14V
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19 when the cell is operated under the CG-assisted mode. Lower OCV means lesser potential
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21 barrier to split H_2O or CO_2 in the CG-assisted mode.
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31 Electrochemical impedance spectra are measured in four different conditions, as shown
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33 in Fig.4 (b). The intercept of the real axis at high-frequency corresponds to ohmic resistance
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35 of the cell, while the real axis range covered by the arc at lower frequency region represents
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37 the overall electrode polarization resistance, including both the anode and cathode
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39 polarization resistances. The total resistance is the sum of the ohmic resistance and the
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41 polarization resistance. As to the ohmic resistance of a cell, it is the sum of the ohmic
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43 resistances of the anode, the electrolyte layer, the cathode, and the contact resistance
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45 between each two adjacent layers. From Fig.4 (b), it can be seen that the intercept of the real
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47 axis is very similar in four different measurement conditions, indicating that the cell ohmic
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49 resistance is almost the same. Since the ohmic resistance is mainly determined by the
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condition of the electrolyte in electrolyte-supported cells, the similar ohmic resistances can be explained by the identical fabrication process of the LSGM electrolyte in all cells tested.

In the conventional mode, the polarization resistance under 150 mA cm^{-2} ($0.389 \text{ } \Omega \text{ cm}^2$) is smaller than that under OCV ($0.517 \text{ } \Omega \text{ cm}^2$), suggesting that the reaction rate can be enhanced with applied current. Comparing the polarization resistance under OCV in the conventional mode and the CG assisted mode, the former ($0.517 \text{ } \Omega \text{ cm}^2$) is smaller than the latter ($0.890 \text{ } \Omega \text{ cm}^2$), which is possibly due to the introduction of the CG process in the anode side (The major gas component in the anode side is found to be CO as shown in Fig.5). In the anode side of CG assisted mode, the produced O^{2-} is consumed by reacting with CO to form CO_2 ($\text{O}^{2-} + \text{CO} = \text{CO}_2 + 2\text{e}^-$). The larger polarization resistance may be caused by the sluggish electrochemical reactivity of CO or the slow rate of “CO shuttle”. Similar to the conventional mode, in the CG assisted mode, the polarization resistance reduces to $0.71 \text{ } \Omega \text{ cm}^2$ when 150 mA cm^{-2} is applied. The larger polarization resistance of the CG assisted mode indicates a larger polarization loss. However, since the significant decrease in the open circuit voltage (i.e., a significant reduction of potential barrier), a much lower overall electrolysis voltage is still achieved for the CG assisted mode for the same current density compared with the conventional mode. Consequently, the consumption of electrical energy can be reduced in the CG assisted mode.

3.3 The analysis of carbon gasification process in the anode side

As shown in Fig.1, in the anode side of the CG assisted mode, carbon source is introduced. Assuming that the amount of carbon is much larger than that of O_2 , the gas atmosphere in the anode side under thermodynamic equilibrium condition can be calculated by HSC 6.0 software, as displayed in Fig.5 (a). Between 600 and 800 K, CO_2 is the major

product, while between 973 K and 1173 K (operation temperature of the CG assisted co-electrolysis in this study), CO becomes the predominant product, suggesting that CO can be obtained in the anode side of this system.

Besides the thermodynamic factors, the kinetics of carbon gasification should also be taken into consideration, because it is crucial for the rate of “CO shuttle” between the solid carbon and the anode, which influences the performance of SOEC. Consequently, the kinetics of carbon gasification in air and CO₂ were studied by thermogravimetric analysis, as shown in Fig. 5(b). From the TG and DTG curves, it can be seen that weight loss of carbon starts at approximately 600 K in the air, while weight loss only starts at about 850 K in CO₂, indicating that carbon has higher reactivity with O₂ than with CO₂. This result also reveals that below 850 K, the major product of O₂ and carbon is CO₂, consistent with the thermodynamic calculation analysis.

Above 1000 K, the DTG curve (carbon in CO₂) shows that the reactivity of carbon with CO₂ increases greatly with increasing temperature and reaches the maximum at 1200 K. Therefore, at 1123 K (the operating temperature of SOEC in this study), the reactivity of carbon with CO₂ is not at the fastest condition. The sluggish reaction could be one of the reasons for the larger polarization resistance of the CG assisted co-electrolysis than that of the conventional co-electrolysis observed in Fig. 4 (b). As the reaction rate increases with increasing temperature, the polarization resistance of the CG assisted co-electrolysis can be reduced by further increasing the operation temperature.

Fig. 5(c) presents the exhaust gas composition in the anode side analysed by GC with 5 ml min⁻¹ N₂ as sweep gas when the device is operated with a constant current density of 300 mA cm⁻². Besides N₂ from the sweep gas, the exhaust gas contains ~10% CO and very small amount of CO₂

(about 0.1%). Thus the gas generated in the anode side is predominantly CO at the operating temperature (1123 K), which is consistent with the results from thermodynamic calculation. It also demonstrates that “CO shuttle” works continuously in the anode side.

3.4 Electricity consumption and energy efficiency of the system

Compared with heat and carbon sources, electricity is a more valuable energy form. When the electrolysis cell is operated at thermoneutral voltage, only a small amount of extra heat (4% of total energy input) is needed. [1] Furthermore, carbon sources (coal and biomass) are typically cheap and abundant. Since electricity cost is the major contributor for the production cost of syngas, the electrical efficiency plays a decisive role in determining the economic competitiveness of this system.

Electricity input per unit of syngas production when the electrolysis cell is operated at -0.4 A cm^{-2} is compared in different mode in Table. 1. In the CG assisted mode, the total electrical energy needed is 13.8 kJ, which is even smaller than 1/15 of the conventional mode (216 kJ). This substantial reduction in electricity consumption is due to two reasons. On one hand, the portion of electrical energy for overcoming the potential barrier is much smaller in the CG assisted mode compared with that in the conventional mode. On the other hand, CO can be produced in the anode side of the CG assisted mode. Consequently, more CO can be produced in the CG assisted mode for the same amount of electricity consumed.

Although it has been shown that the introduction of carbon gasification in the anode side can reduce the potential barrier and electricity consumption of SOECs, the introduction of carbon source increases the input energy and the CG process may lead to useful energy losses since some portion of the chemical energy from carbon is converted into heat instead

of electricity or chemical energy stored in the syngas. Consequently, it is also necessary to evaluate the energy efficiency defined as how much energy is converted to the desirable product.[40-42] The energy efficiency can be evaluated by the ratio of energy output and energy input (the calculation procedure based on the electrochemical and GC data is shown in detail in the supporting material).

The results of efficiency calculation for both modes are shown in Fig.6. The efficiency of the conventional mode increases significantly below 0.4 A cm^{-2} and rises steadily when the current density exceeds about 0.8 A cm^{-2} . This trend is similar to that in the solid oxide steam electrolysis cells [40]. The efficiency curve of the CG assisted mode displays a similar trend, but it is always above the one in the conventional mode. For instance, at an electrolysis current of -0.4 A cm^{-2} , the efficiency of the CG assisted mode (0.64) is 36% higher than that in the conventional mode (0.47). This demonstrates that the introduction of carbon gasification in the anode side significantly improves the total energy efficiency of the co-electrolysis.

4. Conclusion

In summary, we have demonstrated the feasibility of a novel and efficient syngas generator (CG assisted co-electrolysis), in which the carbon gasification and the co-electrolysis are synergistically combined. Compared with the conventional SOECs, the significant distinction of the CG assisted co-electrolysis is the introduction of carbon gasification process in the anode side which can reduce the potential barrier by about 1 V. The most significant point is that the consumption of electrical energy is substantially reduced and the total electrical energy efficiency is significantly increased. Moreover, the operational voltage window is larger in the CG assisted mode. Therefore, CG assisted co-electrolysis shows great promise for eco-friendly and efficient utilization

of coal/biomass and CO₂ to store energy and reduce the emission of CO₂.

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Table and Figure Captions

Table 1 Comparison of electricity consumption for 1 mole syngas production in the CG assisted and conventional mode.

Fig.1 Schematic illustration of carbon gasification assisted solid oxide co-electrolysis.

Fig.2 Thermodynamic calculation as function of temperature for co-electrolysis process (a) conventional mode and (b) CG assisted mode.

Fig.3 The microstructure of single cell (a) SFM-SDC/LSGM/SFM-SDC triple layers; (b) interface of SFM-SDC and LSGM.

Fig.4 (a) *I-V* curves for the electrolysis cells operated in conventional mode and CG assisted mode at 1123K; (b) impedance spectra for electrolysis cells operated in four different conditions.

Fig.5 (a) Thermodynamic equilibrium calculation results for the reaction of 2 mol O₂ with 98 mol carbon at different temperatures; (b) TG and DTG of carbon source in air and CO₂ condition; (c) the exhaust gas composition in the anode side.

Fig.6 *I*-total energy efficiency curves for the electrolysis cell operated in conventional mode and CG assisted mode at 1123K.

Table 1

	Conventional mode	CG assisted mode
Current density (A cm ⁻²)	-0.4	-0.4
Applied voltage (V)	1.12	0.143
Electrical power (W)	0.448	0.0572
Electrical energy (kJ)	216	13.8

Figure

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6