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Scaling up syngas production with controllable H_2/CO ratio in a highly efficient, compact, and durable solid oxide coelectrolysis cell unit-bundle

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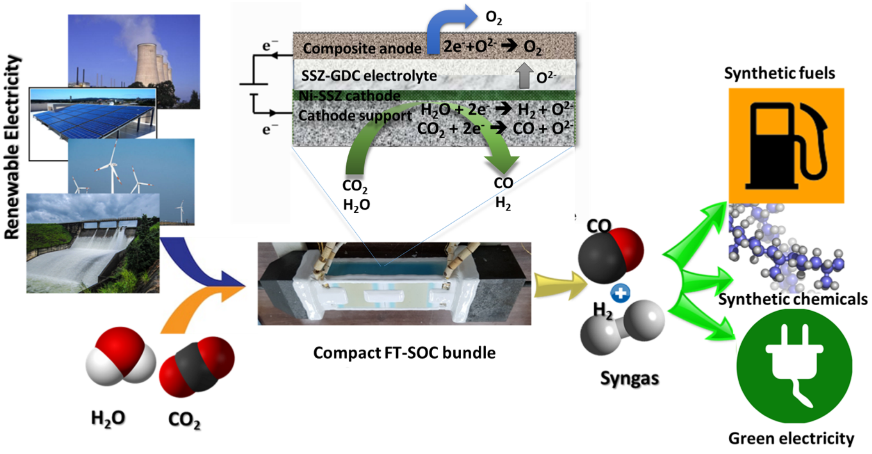
HIGHLIGHTS

- Highly efficient, durable and modular SOC cells and stacks developed.
- Controllable syngas H_2/CO ratio achieved between 1 and 4 with 90% CO_2 conversion.
- A maximum current density of −3.2A/cm^2 at 1.6 V at 800 °C was achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

High-temperature coelectrolysis of H_2O and CO_2 by using solid oxide coelectrolysis cells (SOC) is considered to be among the most efficient processes for CO_2 conversion as these SOCs can efficiently utilize both heat and renewable electrical energy. One of the key components is the development of highly efficient, modular SOC cells and stacks to further scale up the CO_2 conversion process towards industrial applications. In this study, we developed highly efficient and durable flat-tubular solid oxide coelectrolysis cells (FT-SOCs) and investigated the electrochemical performance (I-V, EIS, long-term galvanostatic test) of single cells and a 6-cell bundle for CO_2-H_2O coelectrolysis to produce syngas with controllable H_2/CO ratios. The FT-SOC with an active area of 40 cm^2 reached a maximum current density of −3.2A/cm^2 at 1.6 V at 800 °C and an H_2O/CO_2 ratio of 2. In the 6-cell FT-SOC bundle, 90% CO_2 conversion was achieved by producing high-quality syngas with flexible H_2/CO ratios and

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stable long-term operation for continuous 500 h. The results of this study show that by using an FT-SOC bundle, scalable and controllable syngas quality could be produced and integrated with the multitude of downstream processes.

1. Introduction

Due to massive industrial activities and usage of fossil fuels, the average global carbon dioxide level in the atmosphere is rising at an alarming rate, currently reaching over 400 ppm. Methods of CO_2 reduction/conversion are being sought to avoid the cataclysmic consequences of greenhouse gas accumulation [1]. One of the most effective ways is to convert CO_2 into synthetic chemicals by using renewable electricity from the sun or wind resources [2,3]. High-temperature solid oxide electrolysis cell (SOEC) technology can efficiently split greenhouse gas CO_2 to form CO, which is a raw material for various chemical processes [3,4]. Recently, researchers have focused on the production of syngas (a mixture of CO and H_2) by simultaneous electrolysis of CO_2 and H_2O [4–7]. The syngas mixture can be used as a fuel for clean power generation in power plants and solid oxide fuel cell based power generation systems [8–10]. Syngas produced from the coelectrolysis process is a raw material for the Fischer-Tropsch process. which catalytically produces hydrocarbons from syngas [11]. Another benefit of high-temperature coelectrolysis is that pure oxygen gas is obtained as a byproduct [12]. Although steam reforming and coal gasification have been used commercially to produce syngas, high-temperature coelectrolysis is superior to those technologies due to the fact that it consumes CO_2, which is usually a byproduct of the conventional industrial processes [13]. Compared with low-temperature alkaline electrolysis, high-temperature electrolysis does not require expensive platinum catalysts and needs less electricity due to the high efficiencies of the solid oxide electrolysis system. Hence, SOECs not only serve as a carbon-neutral technology but also provide a cheap and sustainable avenue for storing surplus electricity and waste heat as chemical energies [14,15].

The commercial viability of a high-temperature H_2O/CO_2 co-electrolysis process depends on many factors and the product syngas composition is one of the most deciding factors. For the downstream industrial utilization of the syngas, different ratios of H_2/CO are required for the production of diverse range chemicals. For instance, the Fischer-Tropsch (F-T) process requires a syngas with H_2/CO ratio of 2 to produce synthetic liquid fuels, whereas for the production of aldehydes by the oxo-process (hydroformylation) a H_2/CO ratio of 1 is needed. Similarly, synthetic natural gas (methane) production ($CO + 3H_2 \rightarrow CH_4 + H_2O$) required H_2/CO ratio of 3 [16]. Syngas obtained from commercial natural gas-based reforming process produces syngas with very high H_2/CO ratio and thus needs a downstream process such as a pressure swing absorption (PSA) unit to regulate the required H_2/CO ratio. The extra processing of the syngas increases the operation and maintenance requirements of the syngas production process. H_2O/CO_2 co-electrolysis in high-temperature solid-oxide cells can potentially produce high-quality syngas with controllable composition in a single module. The H_2/CO ratio of the syngas obtained by H_2O/CO_2 co-electrolysis depends on numerous factors such as operating voltage and current density of the cell, cathode feed gas H_2O/CO_2 ratio, process temperature, and the electrode material properties and microstructures [15]. Although substantial work has been done by many research groups on synthesizing new SOC cathode materials and designing efficient cells and stacks, only a few studies have considered the issue of syngas product composition control and distribution [16]. Further studies are required to moving a step further toward technological feasibility through improved electrode materials, novel cell design, and versatile product syngas quality, the synthetic fuels and chemical produced based on SOC high-temperature coelectrolysis technology could become economically competitive with the conventional fossil fuel utilization technologies.

The structural characteristics and geometric design of the co-electrolysis cell determine the performance of the syngas production system as well as the quality of the product. High-temperature solid oxide-based coelectrolysis cells (SOC) can be manufactured into planar, tubular, flat-tubular configurations [6,12,17–30]. The planar SOCs offers higher power density as compared to the tubular SOCs, but their disadvantage is that for large area cells, the thermal stresses present between the sealing material and the cell components tend to induce higher degradation and cell-to-cell sealing is also difficult. On the other hand, the tubular solid oxide coelectrolysis cells are easily sealed offer higher resistance to thermal expansion stress but scale-up of the tubular cells is a challenging task due to current collection difficulties and lower power density per unit area [21,22,27,31–37]. The flat-tubular SOC cell combines the advantages of both the planar and tubular cells, and has an appropriate power density and good mechanical strength and multiple cells can be easily configured to stack and system [37–41].

Another challenge for the commercialization of high-temperature coelectrolysis is degradation of the SOC components during the long-term operation. Many literature reports suggest severe degradation in the performance of the cells due to delamination of the air electrode [42–45]. One of the approaches to reduce the degradation in SOC during long-term operation is to use high oxygen capacity double perovskites which not only achieve higher efficiency but also eliminate degradation in solid oxide electrochemical cells [46].

For a commercially competitive H_2O/CO_2 coelectrolysis technology, it is very important to increase the gas production capacity of the coelectrolysis system by scaling up the cells to a unit-bundle, short stack and subsequently, and for also for a practical system, a long-term thermal stability of 5–10 years under actual operating conditions is required. Furthermore, in order to improve the electrochemical output of the coelectrolysis reaction in a single cell, the active area of the cell must be enlarged. Therefore, scale up to a unit-bundle and stack is imperative for the commercialization of high-temperature coelectrolysis technology.

In this study, we have developed high performing, large area flat-tubular SOCs. The performance of a flat tubular solid oxide coelectrolysis cell (active area 40 cm2) and 6-cell unit-bundle is investigated. Our FT-SOCs showed significantly higher electrochemical performance owing to improved microstructure and layer-by-layer fabrication process and novel current collection on the FT-SOC enhancement of the performance is achieved flat-tubular cells and a compact and robust 6-cell module has been designed, fabricated and tested under various operating conditions to produce a controllable quality of syngas. It has been observed that the H_2/CO ratio of the produced syngas can be controlled by tuning the applied current and the inlet feed gas composition in the FT-SOC unit-bundle. The FT-SOC unit bundle was also tested for long-term durability during 500 h continuous operation. The scale-up of coelectrolysis system from a single cell to unit-bundle with the capability of direct integration into industrial processes of syngas utilization has been investigated, thus providing vital data for the high-temperature solid oxide coelectrolysis technology development.

2. Experimental

2.1. Fabrication of flat-tubular solid oxide cells (FT-SOC)

The flat-tubular fuel electrode supports for FT-SOCs were fabricated as described in [47]. Briefly, the flat-tubular cathode supports were extruded from a well-mixed and kneaded mixture of NiO-8YSZ powder with pore former (carbon black), distilled water, and organics