Journal of Power Sources 273 (2015) 1202–1217

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

A low-temperature co-fired ceramic micro-reactor system for high-efficiency on-site hydrogen production

Bo Jiang [a, b], Thomas Maeder [b], Alejandro J. Santis-Alvarez [c], Dimos Poulikakos [c], Paul Muralt [a, *]

[a] Ceramics Laboratory, EPFL, Lausanne, Switzerland
[b] Laboratory of Micro-engineering for Manufacturing, EPFL, Lausanne, Switzerland
[c] Laboratory of Thermodynamics in Emerging Technologies, ETH Zurich, Zurich, Switzerland

HIGHLIGHTS

- Novel high-temperature micro reaction system based on the LTCC technology.
- Demonstrated on-site, self sustained syngas production for micro SOFC applications.
- Built-in heater for ramping up temperature.
- Excellent thermal insulation, low power dissipation of integrated system.
- Well distributed flow inside micro reactor for high reforming efficiency.

ARTICLE INFO

Article history:
Received 28 April 2014
Received in revised form
2 September 2014
Accepted 11 September 2014
Available online 19 September 2014

Keywords:
LTCC
Micro-reactor
Hydrogen production
Solid oxide fuel cells

ABSTRACT

A ceramic-based, meso-scale fuel processor for on-board production of syngas fuel was demonstrated for applications in micro-scale solid-oxide fuel cells (μ-SOFCs). The processor had a total dimension of 12 mm × 40 mm × 2 mm, the gas reforming micro reactor occupying the hot end of a cantilever had outer dimensions of 12 × 18 mm. The device was fabricated through a novel progressive lamination process in low-temperature co-fired ceramic (LTCC) technology. Both, heating function and desired fluidic structures were integrated monolithically into the processor. Using catalytic partial oxidation of a hydrocarbon fuel (propane) as a reaction model, a thermally self-sustaining hydrogen production was achieved. The output flow is sufficiently high to drive an optimized single membrane μSOFC cell of about the same footprint as the micro reactor. Microsystem design, fabrication, catalyst integration as well as the chemical characterization are discussed in detail.

1. Introduction

Electrical power supplies for portable electronic devices are subject to important challenges, as current battery technologies cannot raise energy density at the pace of increased power consumption in portable applications. As a consequence, the autonomy of devices such as smart phones, digital cameras, etc. is rather limited. An alternative technology is to store energy in chemical form as a fuel, and then to convert fuel into electrical energy by means of fuel cells. Even if considering an overall fuel cell system efficiency of 15% only, the achievable output energy densities (e.g. ~7.4 MJ kg^{-1} for propane, ~3.0 MJ kg^{-1} for methanol) are greatly larger than the ones of Li-ion batteries (~0.9 MJ kg^{-1}) [1,2]. Therefore, mesa or micro fuel cells are currently studied and developed intensively as a replacement of batteries. Micro-scale solid-oxide fuel cells (μ-SOFCs) appear to be very promising, because they exhibit higher efficiencies and a better compatibility with chemical fuels (no CO poisoning issue) as compared to proton-exchange membrane fuel cells. The μ-SOFCs require, however, much higher operating temperatures of over 400 °C to achieve meaningful power densities. To avoid carbon coking at electrode materials, it is preferred to reform the hydrocarbon fuels (e.g. propane) into syngas (H_2 + CO) with an on-site fuel processor. Current reforming technologies for on-site syngas production include steam reforming (SR), catalytic partial oxidation (CPOX) and auto-thermal/oxidative steam reforming (ATR/OSR) [3,4].

In μ-SOFCs, such an on-site reforming process cannot be carried out in a large conventional reactor because of the following

---

* Corresponding author. Tel.: +41 21 6934957; fax: +41 21 6935810.
E-mail address: paul.muralt@epfl.ch (P. Muralt).

http://dx.doi.org/10.1016/j.jpowsour.2014.09.084
0378-7753/© 2014 Elsevier B.V. All rights reserved.

requirements: (i) compact and miniaturized integration into μ-SOFCs, (ii) accurate control of reforming reactions, and (iii) short start-up time and rapid transition to off-state mode. The micro-reactor technology is widely considered as a robust solution for on-site hydrogen production from hydrocarbon fuels [2,4]. The dramatic reduction of characteristic lengths within micro-reactors greatly enhances mass and heat transport, minimizes catalyst materials, improves process stability against thermal runaway, and thus facilitates process control. Last but not least, micro reactors can be realized with dimensions in the millimetre range, which is the right size for integration in μ-SOFCs devices.

To date, various micro-reactors for on-site syngas production have been developed [5–11]. Microchannel and packed-bed types of micro-reactors fabricated from stainless steels have been used for the SR of methanol operated in a temperature range of 250 °C–450 °C [6]. Despite their advantages, such as easy machining and high mechanical strength, the metal-based micro-reactors are limited in downscaling by their high thermal conductivity, and lower power-to-mass ratio because of their high density. Alternatively, silicon-based microfabricated micro-reactors were studied for fuel reforming processes, for instance, for high-temperature (>400 °C) CPOX processes of methane [5]. High-resolution micro fabrication enables fine structures that improve heat transfer, for instance by using a suspended-tube configuration [12], while simultaneously providing fluidic functional structures, such as stoppers for easy catalyst installation [13]. Moreover, heating elements and temperature sensors can be integrated via thin-film technology for monitoring and control of the chemical process. However, major difficulties are encountered with silicon based microreaction systems. Firstly, silicon is thermo-mechanically incompatible with most materials that are used in micro solid oxide fuel cells: the coefficient of thermal expansion (CTE) in silicon and common μ-SOFC building materials are 3×10^{-6} K^{-1} and 10×10^{-6} K^{-1} respectively [1], and thus differ considerably. Silicon is a good heat conductor, and thus cannot serve to bridge the device to a (cold) housing. In addition, silicon technology is rather expensive.

For these reasons, we recently proposed ceramic- and glass-based micro-reactors for high-temperature reforming reactions [9,14–16]. Hotz et al. [9] developed a disk-shaped micro-reactor made of quartz glass and achieved high selectivity of H_2 (92%) and CO (82%) species via CPOX of butane at 550 °C. In a previous work [14,17], we developed an aluminoborosilicate glass-based micro hot plate on which a micro reformer for syngas production was integrated by glass sealing. Its efficient thermal decoupling allowed a thermally self-sustaining CPOX syngas production above 500 °C, and served to demonstrate an integrated μ-SOFC unit for producing a power density of 50 mW cm^{-2} at ~550 °C. However, the utilized glass materials system (especially the sealing glass) was found to be somewhat fragile to thermal shock under operation cycles, which we ascribed to high thermal gradients and resulting mechanical stresses arising from the low thermal conductivity of glass. In addition, glass seals for joining fluidic components (e.g. the micro-reactor chamber) are problematic, and silicate glasses are not easy to machine. We thus focused on ceramic-based micro-reactors. These are intrinsically more suited for on-site syngas production because ceramics exhibit (i) an excellent chemical resistance; (ii) a higher mechanical strength than the used glass material; and (iii) a thermal conductivity that can mitigate hot-spot formation. Both (ii) and (iii) allow in turn selection of materials with higher CTE that is matched with μ-SOFC materials.

Among ceramic technologies, low-temperature co-fired ceramic technology (LTCC) enables production of micro-reactors in a fast prototyping approach and at low cost [7,8,18]. A typical LTCC fabrication process involves mechanical structuration of LTCC green tapes (unfired state) and integration of thick-film functional materials via screen printing technologies. Afterwards, all tapes are stacked and laminated together under a hot pressing process (~70 °C). This laminate is sintered in a one-step process at temperatures of 850 °C–900 °C to form a monolithic and rigid ceramic module. In our case, such a module aims at having integrated functional materials and embedded 3-dimensional fluidic structures with optimized heat transfer properties and miniaturization. The LTCC technology is considered as a very attractive solution for functional packaging in μ-SOFC applications because of its easy and low-cost fluidic structuration processes, its high material stability, and good compatibility with thick-film technology. The CTE of LTCC material is generally higher than that of silicon, in fact close to materials of an oxide fuel cell membrane, but with a CTE mismatch issue when the latter are inside a silicon frame. However, this problem can be overcome by a metallic hermetic bonding that joins silicon and ceramic materials, as explored in Refs. [19,20]. Park et al. [8] has demonstrated a fully integrated fuel processor for the hydrogen production via the SR of methanol. This system included several fluidic components such as a vaporizer, a SR reactor, a heat exchanger and a preferential CO oxidation (PrOX) reactor, producing about 0.26 W in terms of hydrogen chemical energy (at 300 °C) for the fuel cells. Furthermore, Belavič et al. [18] reported a multifunctional LTCC-based fuel processor that combined both fluidic components such as an evaporator, steam reformer, a combustor and additional heating/sensing functions i.e. thick-film heating element and pressure gauges.

Previous work clearly showed the promising potential of micro-reactors for on-site hydrogen (or syngas) production. However, published literature on integrated micro reactor systems able to deliver thermally self-sustaining syngas production in a plug-and-play manner is still scant. Therefore, we present here a meso-scale LTCC-based micro-reforming system for on-site syngas production. The CPOX of propane (Reaction (1)) was chosen for this study due to the abovementioned BOP advantages over SR/OSR that no complex water management was required and it easily achieved a thermally self-sustaining reforming process) [21]. The used catalyst in this study, composed of rhodium (Rh) and $(Ce,Zr)O_2$ nanoparticles, has demonstrated a high syngas yield as well as a high resistance to coke formation in the temperature range of 400–700 °C [22]. The advantage of LTCC technology lies in its flexibility to realize micro-fluidic structures such as channels, its integration of temperature sensors as well as heating elements. Besides, LTCC remains an economic fabrication technology. The main highlights of this work are:

- Demonstration of a millimetre-scale LTCC micro-reactor ($40 \times 12 \times 1.8$ mm^3) for the on-site syngas production via the CPOX of propane at above 500 °C in a thermally self-sustaining manner; a process that is advantageous from a balance-of-plant (BOP) perspective for small devices, as it obviates the need of both an auxiliary heat source and a water management accessory.
- The new lamination process for integrating fine fluidic structures within the micro-reactor;
- The effect of a thick-film metallic thermal spreader for improving thermal uniformity and syngas production performance of the LTCC reactor;
- A novel symmetric cross-flow design for improved syngas yields within the LTCC micro-reactor.

2. System design

2.1. Thermal management

The thermal management plays a critical role to the efficiency of high-temperature micro-reactor systems. Downscaling is