Journal of Power Sources 402 (2018) 124–132

Contents lists available at ScienceDirect

Journal of Power Sources

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

A robust flat-chip solid oxide fuel cell coupled with catalytic partial oxidation of methane

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HIGHLIGHTS

- A flat-chip configuration of SOFC was proposed.
- A catalytic partial oxidation (CPOX) reformer was coupled to pretreat hydrocarbon.
- Flat-chip SOFC can survive harsh temperature change rate well above 200 °C·min^{-1}.
- Flat-chip SOFC with CPOX endured repetitive redox cycling at least 23 times.

ARTICLE INFO

Keywords:
Catalytic partial oxidation
Flat-chip SOFC
Redox cycling
Thermal cycling

ABSTRACT

This study demonstrates a module that consists of solid oxide fuel cell (SOFC) with flat-chip configuration and a catalytic partial oxidation (CPOX) reformer. The CPOX reformer uses Rh supported by Al_2O_3 as catalyst and functions effectively. The optimized temperature of CPOX reformer is 800 °C and the optimal C/O ratio to operate the reformer is ca. 0.8 where the maximum reforming efficiency, i.e. 86.1% can be obtained. The CPOX reformer can be coupled with a flat-chip SOFC, which is advantageous for its good thermal shock resistance, quick startup and good response characteristics. The flat-chip SOFC is able to function with a temperature difference over 850 °C across the cell itself and can survive the harsh tests of rapid thermal cycling with the temperature change rate well above 200 °C·min^{-1}, and repetitive redox cycling at least 23 times.

1. Introduction

Solid Oxide Fuel Cell (SOFC) can be applied in a combined heat and power (CHP) system to generate multiple forms of useful energy with high efficiency, sequentially or simultaneously [1–3]. An SOFC-based CHP system, due to its advantages in realizing small scale, high efficiency over a broad range of load profiles and low emissions, has a potential prospect to be applied as remote and distributed power supplier [1,4–6].

Fig. 1 illustrates the process design of a CHP system based on SOFCs. Methane and air/water steam are premixed and fed into a reformer. The reforming gas enters into the SOFC anodes while air flowing over the cathodes. The electricity produced is utilized by a power controlling system. Unreacted reforming gas is combusted with addition of fresh air before emission. The heats generated by the combustor and the reformer are used for external application and to preheat the reactants. With a heat management system, the overall system can be self-sustainable.

Though SOFC can be fed with varied fuels, its efficiency is subject to inlet fuel composition and direct application of hydrocarbon leads to carbon deposition [7]. Therefore, a reformer that converts hydrocarbons to synthesis gas is required by a SOFC based CHP system. The popular methods of reforming include steam reforming (SR), dry reforming (DR) and partial oxidation (POx) [8]. Both SR and DR are strongly endothermic, which increases energy consumption and device complexity. POx needs high operating temperature in the range of

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https://doi.org/10.1016/j.jpowsour.2018.09.017
Received 28 May 2018; Received in revised form 13 August 2018; Accepted 6 September 2018

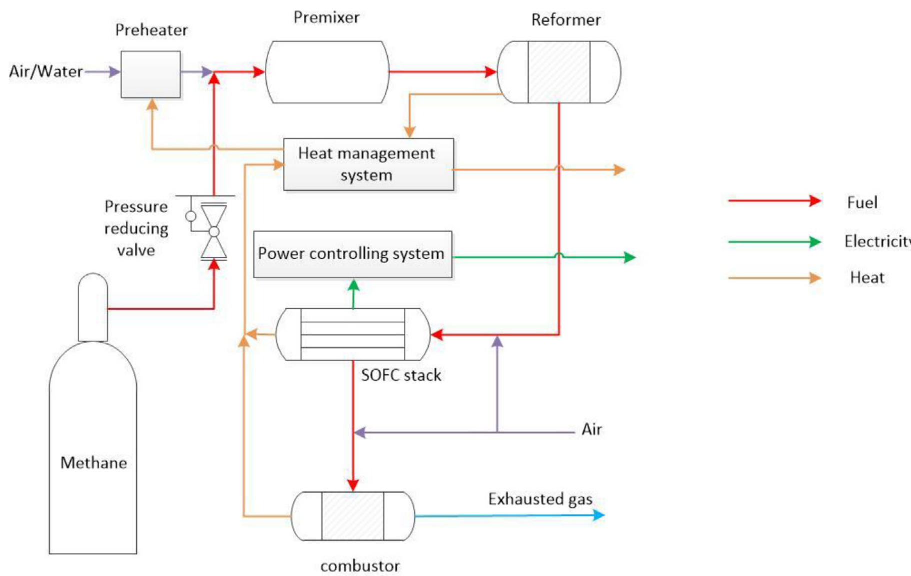

Fig. 1. Process design of a SOFC based CHP system.

Table 1
Enthalpy of possibly important reactions in a CPOX process [10,11].

	Reaction	Δ_rH(kJ/mol,298 K)	
Catalytic partial oxidation	$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	−35.5	(1-1)
Combustion	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	−801.7	(1–2)
Steam reforming	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	+206.1	(1–3)
Dry reforming	$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	+247.5	(1–4)
Water gas shift	$CO + H_2O \rightleftharpoons CO_2 + H_2$	−41	(1–5)

1000–1500 °C [9], due to the low reaction rate. Catalytic partial oxidation (CPOX) therefore attracts attention in recent years for its advantages of inherently rapid reforming kinetics with quick start-up and response characteristics [10]. Table 1 shows the enthalpy of possibly important reactions in a CPOX process where the heat demanded by reforming reactions can be at least partially compensated by the exothermic reactions, making it ideal to be applied with high temperature fuel cells like SOFC [11].

Finnerty et al. [12] investigated the SOFC system equipped with a catalytic fuel processing system, which comprised of a Ru-based pre-reformer and a Pt-based combustion zone. In the Ru-based pre-reformer, the catalytic partial oxidation reaction took place and the fuel was converted into synthesis gas. The unutilized fuel was combusted in a Pt-based combustion zone, generating heat to preheat the inlet fuel fed into the pre-reformer and SOFC. The result showed that the system functioned well with good thermal and electric performance of around 8 W_e, and could be warmed up in 5 min. The CPOX was also seen to be successfully applied on CHP systems in other researches [13–15].

For the portable application, a SOFC-based CHP system prefers rapid start-up, which means the SOFC operating around 600–1000 °C [16] has to survive in rapid temperature change, i.e., resistant to thermal shock. That, however, is really challenging to present SOFC technologies, which usually requires a slow temperature variation below 5 °C/min during start-up and cool-down. The prevailing configurations of SOFC includes planar and tubular designs. Planar cell has a simple structure and is favored in practice for virtues of higher power density and easy-stacking. However, it is very difficult for planar SOFCs to survive in rapid temperature change. In a planar SOFC stack, stack components made of varied materials including ceramic cells, glass sealing rings and metallic interconnectors are assembled in sequence. Matching the properties of these components such as thermal expansion and geometry integrity is not easy and the matching solution usually is awkward and costly, especially for applications undergoing moderate or rapid temperature change, which actually in most of cases is the major reason causing the failure of a SOFC stack. In the tubular design, stack reliability is improved as the cell sealing is to a large extent realized by the closed and gas-tight electrolyte, i.e., no extra sealing component is required and the strict matching requirement of sealing is therefore mitigated [16–18]. The challenges of tubular design include controlling the precision of the cell geometry [19,20], e.g. the straightness along a long tube, say above 500 mm and the roundness of the cross section during scale-upped cell fabrication, and stacking, i.e. connecting the electrode of one cell to the electrode of another cell. Note that tight electrode contacting and consistent cell geometry among cells is vital to reduce stack internal resistance and enable standardized stack manufacturing and assembly.

As an attempt to combine the advantages of tubular and planar designs, a prototype SOFC of flat-chip configuration is proposed and evaluated in this study. In this design the cell in general take a planar configuration, facilitating tight electrode contact and well cell geometry control during manufacturing scale-up. Besides, the gas channels are surrounded by the same material of zirconia as that of the electrolyte, i.e. no extra sealing component is needed as the tubular design. Thermal expansion matching between sealing glass, ceramic cell and metallic interconnector that had to be strictly satisfied in normal planar cell design is thus avoided, enabling the flat-chip cell more tolerant to rapid temperature change. The electrodes of the flat-chip cell are electrically connected to the pads at the far ends that during operation stay at temperature below 200 °C, similar to that of the tubular configuration again. Stacking of the flat-chip cells will be carried out via connecting the electrode pads at low temperature below 200 °C. As the process of the flat-chip cell fabrication is similar to that of the multiple layered integrated-circuit production, it has the potential to support massive and completely automatic manufacturing with high reproducibility. The flat-chip cell has been verified sufficiently robust and able to survive in repetitive redox cycling and fast thermal cycling of temperature change rate well above 200 °C·min^{-1}. The cell was also seen to be functional with methane input when equipped with a specially developed CPOX reformer, whose electrochemical performances would be mainly discussed in this study.