



# Direct methane solid oxide fuel cells based on catalytic partial oxidation enabling complete coking tolerance of Ni-based anodes



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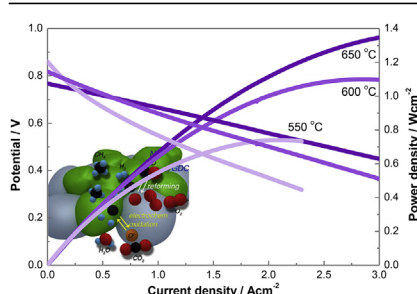
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## HIGHLIGHTS

- Direct CH<sub>4</sub> fueled SOFCs operated via catalytic partial oxidation are demonstrated.
- A high performance of 0.74 W cm<sup>-2</sup> at 550 °C is achieved.
- Enhanced CH<sub>4</sub> conversion suggests a promising internal reforming by CPOX.
- Adsorption dynamics on Ni catalysts is elucidated.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Solid oxide fuel cells (SOFCs) can oxidize diverse fuels by harnessing oxygen ions. Benefited by this feature, direct utilization of hydrocarbon fuels without external reformers allows for cost-effective realization of SOFC systems. Superior hydrocarbon reforming catalysts such as nickel are required for this application. However, carbon coking on nickel-based anodes and the low efficiency associated with hydrocarbon fueling relegate these systems to immature technologies. Herein, we present methane-fueled SOFCs operated under conditions of catalytic partial oxidation (CPOX). Utilizing CPOX eliminates carbon coking on Ni and facilitates the oxidation of methane. Ni-gadolinium-doped ceria (GDC) anode-based cells exhibit exceptional power densities of 1.35 W cm<sup>-2</sup> at 650 °C and 0.74 W cm<sup>-2</sup> at 550 °C, with stable operation over 500 h, while the similarly prepared Ni-yttria stabilized zirconia anode-based cells exhibit a power density of 0.27 W cm<sup>-2</sup> at 650 °C, showing gradual degradation. Chemical analyses suggest that combining GDC with the Ni anode prevents the oxidation of Ni due to the oxygen exchange ability of GDC. In addition, CPOX operation allows the usage of stainless steel current collectors. Our results demonstrate that high-performance SOFCs utilizing methane CPOX can be realized without deterioration of Ni-based anodes using cost-effective current collectors.

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## 1. Introduction

Mitigating greenhouse gas emissions in view of the increasing global energy demands has become a major priority for our society [1]. A hydrogen economy solely utilizing water-derived hydrogen as

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a universal energy carrier has been regarded as a promising sustainable model. However, the current technologies of hydrogen production using renewable energy sources are not mature enough to provide the required amount of hydrogen [2,3]. In this respect, utilization of the currently available hydrocarbon fuels is still necessary to meet the current and forecast energy demands [3,4]. Specifically, methane ( $\text{CH}_4$ ), as a major constituent of the widely dispersed natural gas, has attracted considerable attention due to its relative abundance and low emission profile [5,6]. However, the exploitation of  $\text{CH}_4$  via conventional combustion restricts its conversion efficiency to well below the Carnot efficiency, being accompanied by significant  $\text{CO}_2$  emission per unit energy [7,8]. In this respect, the efficient conversion of  $\text{CH}_4$  into usable energy is an important prerequisite to satisfy the requirements of both energy demand and low emission.

Solid oxide fuel cells (SOFCs) can help in the clean and efficient utilization of  $\text{CH}_4$  due to their unique fuel flexibility [2,4,6]. SOFCs feature oxygen ion conductors as an electrolyte, mediating the oxidation of any fuels, from hydrogen to hydrocarbons, by oxygen ions. In this way, direct utilization of  $\text{CH}_4$  in SOFCs without an external reformer can help achieve a maximum theoretical efficiency above 90% and an actual system efficiency of above 65% [2,6], which becomes even higher with combined heat and power (CHP) applications. This can dramatically reduce the  $\text{CO}_2$  emission per unit of produced energy without concomitant  $\text{NO}_x$  generation. Furthermore, the conversion system can be significantly simplified and made more affordable due to the absence of an external reformer, which is a pivotal factor, particularly for small grids or housing systems [4]. Thus, direct  $\text{CH}_4$ -fueled SOFCs can be an interim system for efficient and low-emission utilization of  $\text{CH}_4$  while fully exploiting its current production and transportation infrastructures.

The catalytic and/or electrocatalytic oxidation of  $\text{CH}_4$  occurs at the anode of SOFCs composed of a Ni-yttria stabilized zirconia (YSZ) composite, where Ni serves as an (electro)catalyst and an electronic conductor, while YSZ acts as a catalyst support and an oxygen ion conductor. At a typical SOFC operation temperature (600–1000 °C), Ni is capable of reforming  $\text{CH}_4$  into syngas (a mixture of  $\text{H}_2$  and CO) via catalytic oxidation (i.e., steam reforming, carbon dioxide reforming, or partial oxidation). A mixture of  $\text{CH}_4$  and steam is usually fed to the Ni-based anodes, producing syngas that undergoes further electrochemical oxidation, which is known as internal steam reforming [9–11]. However, the deposition of carbonaceous compounds during internal reforming inevitably deactivates the Ni catalyst [11,12]. In particular,  $\text{CH}_4$  cracking on the Ni catalyst actively takes place above 700 °C, leading to carbon coking-induced catastrophic failure and restricting long-term operation [13,14]. Moreover, internal steam reforming requires considerable amounts of water to be supplied with fuel to reduce carbon coking, which causes an open circuit voltage (OCV) loss due to fuel dilution [15–17]. In this regard, preventing carbon coking in  $\text{CH}_4$ -fueled SOFCs has been a major obstacle for their full exploitation.

Significant efforts have been made to address the coking-induced anode deactivation during the internal reforming of  $\text{CH}_4$  [6,17–25]. Incorporating  $\text{CeO}_2$  or doped  $\text{CeO}_2$  into Ni-based anodes helped to oxidize the carbonaceous adsorbates on Ni surfaces owing to the oxygen exchange capability of  $\text{CeO}_2$ . Since the first demonstration of yttrium-doped ceria (YDC) as a surface carbon oxidation catalyst [26], this approach was combined with a precise control of the  $\text{CH}_4$  flow rate to minimize carbon coking, resulting in a further improved power density [27–30]. Similarly, the introduction of a diffusion barrier consisting of partially stabilized  $\text{ZrO}_2$  and  $\text{CeO}_2$  at the inlet side of the anodes was also suggested to reduce the  $\text{CH}_4$  concentration at the anode and increase the

reforming rate [31,32]. In addition, the Ni-doped ceria composites have been utilized the anodes for direct utilization of  $\text{CH}_4$  in the form of nano-composites or additional metal (Sn, Ru or W)-incorporated composites improving the cell stability and performance [29,33–37]. Despite these efforts, it is generally accepted that Ni-based anodes catalyze  $\text{CH}_4$  cracking, inevitably leading to the carbon coking problem, especially in large-scale applications.

In this regard, Ni-free anodes have been developed to avoid the use of the Ni catalyst. Although  $\text{CeO}_2$  was suggested as a sole catalyst for  $\text{CH}_4$  oxidation, utilizing its lattice oxygen, it suffered from low  $\text{CH}_4$  conversion [38,39]. The electrochemical oxidation of  $\text{CH}_4$  was demonstrated to electrochemically furnish oxygen ions via Faradaic control of the reaction rate to compensate for the insufficient oxygen supply [17,28,40]. Perovskite-type mixed ionic-electronic conducting oxides such as  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ ,  $\text{Sr}_2\text{MgMoO}_{6-\delta}$ , and  $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$  have been developed for this purpose, demonstrating good tolerance toward carbon coking at a high current load condition at which sufficient oxygen ions were provided [41–43]. Despite the remarkable improvements of oxide catalysts, complete  $\text{CH}_4$  conversion using this methodology is hardly achievable without the Ni catalyst, considering the low power densities of 0.2–0.44  $\text{W cm}^{-2}$  at 800–900 °C obtained for oxide catalyst systems.

From this perspective, the catalytic partial oxidation (CPOX) of  $\text{CH}_4$  on a Ni catalyst can be an alternative approach to address the carbon coking issue and simultaneously achieve a high conversion of  $\text{CH}_4$ . Although there is no consensus on the atomistic mechanism of  $\text{CH}_4$  reforming on supported metal catalysts, it is accepted that the carbonaceous adsorbates are readily oxidized by the chemisorbed oxygen species on the metal surface, which are generated from either co-fed oxidants (including  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{O}_2$ ) or the lattice oxygen supplied by oxide supports [44–46]. Since the surface oxygen is mainly responsible for the elimination of adsorbed carbon, it can be inferred that  $\text{O}_2$  should be more effective than other oxidants due to its ease of dissociation. Thus, the CPOX of  $\text{CH}_4$ , in which half a mole of the  $\text{O}_2$  oxidant is supplied to  $\text{CH}_4$  for a stoichiometric reaction, can possibly prevent carbon coking. However, the CPOX approach has rarely been applied to SOFC anodes, since the partial pressure of oxygen in the chamber should be maintained below  $10^{-18}$  atm to develop an electrochemical potential gradient that triggers SOFC operation. In addition, the introduction of high concentrations of  $\text{O}_2$  into the anode chamber may induce Ni oxidation [47,48]. We have recently demonstrated the optimum microstructures for the CPOX operation of Ni-YSZ anodes [49]. Our work suggested a quantitative evaluation of composite anodes, which was used to study the requirements for continuous and stable operation of the Ni-based anodes under CPOX conditions, representing the possibility of robust CPOX operation without carbon coking and Ni oxidation.

Herein, we demonstrate robust CPOX-based SOFCs fueled by  $\text{CH}_4$ , circumventing carbon coking and Ni oxidation. The presence of gaseous oxygen in the anode chamber fundamentally prevents carbon coking, while the oxidation of Ni is prevented with the aid of (electro)catalytic reaction controls and oxygen ionic conductors. The resistance of a stainless steel current collector to carbon coking is also demonstrated under CPOX operation, which is essential for the cost-effective design of large-scale SOFC stacks. Electrochemical evaluations in conjunction with *ex situ* surface analyses prove the feasibility of coking-free and oxidation-resistant Ni-based anodes, enabling durable methane-fueled SOFCs. To the best of our knowledge, our novel approach allows us to achieve direct  $\text{CH}_4$ -fueled SOFCs with long-term stability and the highest performance.

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