



Single-chamber solid oxide fuel cells with nanocatalyst-modified anodes capable of *in situ* activation



Guangming Yang^a, Chao Su^{a,b,*}, Wei Wang^a, Ran Ran^a, Moses O. Tadé^b, Zongping Shao^b

^a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry & Chemical Engineering, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing 210009, China

^b Department of Chemical Engineering, Curtin University, Kent Street, Bentley, Perth, WA 6845, Australia

HIGHLIGHTS

- *In situ* activation of single-chamber SOFCs is realized using CH₄–O₂ mixture.
- Impregnation method was applied for preparing nanocatalysts-modified anodes.
- High power densities and OCVs were obtained for nanocatalysts-modified cells.
- CeO₂ nanoparticles in the anode retained similar morphology after the test.
- CeO₂ was the best choice for the single-chamber SOFC anode modification.

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ABSTRACT

Practical applications of single-chamber solid oxide fuel cells (SC-SOFCs) are partially limited by the difficulties and complications associated with the initialization process, which mainly involves the reduction of NiO to Ni in the anode. Here we propose a facile approach to the *in situ* activation (initialization) of SC-SOFCs with a state-of-the-art sintered nickel-based anode using a methane–oxygen gas mixture, combined with the introduction of nanocatalysts into the anode. RuO₂, CeO₂ or Co₃O₄ with the high activity for methane oxidation are investigated for above purpose. XRD results demonstrate that the nanocatalysts are successfully introduced into the anode *via* a simple solution impregnation technique. Using FESEM, different nanoparticle morphologies are observed for the three catalysts. The time dependence of the cell voltage operating on the methane–oxygen gas mixture demonstrates successful activation following nanocatalyst introduction. Single cells with different nanocatalyst-modified anodes, initialized by *in situ* reduction, deliver high open circuit voltages of approximately 1.0 V and significant peak power outputs of approximately 1000 mW cm⁻² at a furnace temperature of 650 °C. XRD and FESEM analysis indicates that only the CeO₂ retains a same structure and morphology after the test. It suggests that the CeO₂ nanocatalyst is the most promising for practical applications.

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1. Introduction

Single-chamber fuel cells (SCFCs), also called mono-chamber fuel cells, are distinguished from other types of fuel cells by their unique cell configuration, *i.e.*, the cells are operated in a sealing-free mode in which a fuel-oxidant gas mixture is applied as the atmosphere for both electrodes and where the structure is assembled in a single-gas chamber [1,2]. The operating principle of SCFCs relies

on the different catalytic activity and selectivity of each electrode toward the gas mixture [3]. Although low-temperature fuel cells, such as polymer electrolyte membrane fuel cells, are sometimes operated in a single-chamber mode [4], significant safety concerns exist, because such configurations require hydrogen as the fuel, and the direct mixing of hydrogen and oxygen is extremely dangerous. Thus, single-chamber solid oxide fuel cells (SC-SOFCs) are attracting the most attention from researchers at present, because these configurations can use significantly more stable hydrocarbons as their fuel sources [5].

In comparison to the conventional dual-chamber SOFCs, SC-SOFCs allow rapid heating and cooling, simple cell and stack configurations, and simplified gas delivery systems. Therefore, SC-

* Corresponding author. Department of Chemical Engineering, Curtin University, Kent Street, Bentley, Perth, WA 6845, Australia. Tel.: +61 892669709; fax: +61 892662681.

E-mail address: chao.su@curtin.edu.au (C. Su).

SOFCS are promising for applications as portable power sources, although some doubts regarding the practical application of SCFCs have also arisen among the community, in light of the typically poor fuel efficiency of this design. Today, SC-SOFCs have attracted new interest for the co-generation of electricity and chemicals from fuels, which offer the advantages of insensitivity to the polarization current and zero emission, compared to the conventional dual-chamber SOFCs [6,7]. This development solves the problem of using low-fuel-efficiency SC-SOFCs as sole power generating units, because all of the energy that is not converted to electricity by the SC-SOFCs can be stored in chemicals.

Until recently, research activities on SC-SOFCs have been mainly focused on cell performance improvement and the optimization of micro-fabrication processes, while a critical application step of SC-SOFCs, *i.e.*, the activation (initialization) process, has been overlooked [8–13]. Here, activation (initialization) means the creation of the electrocatalytic and catalytic activities of the anode toward the fuel-oxidant mixture through the *in situ* reduction of inert NiO in the anode to metallic Ni [14]. Because the fabrication of SOFCs is typically performed in air, the nickel in the anode is in an oxidized state, leaving almost no activity for the partial oxidation of hydrocarbons to syngas (a mixture of CO and H₂), as well as the electrochemical oxidation of H₂, CO and hydrocarbons; further, only small electronic conductivity of the anode remains. Hence, the anode should be reduced to achieve successful operation for power generation applications. In the dual-chamber configuration, the activation step is very simple, where diluted hydrogen is introduced into the anode chamber at relatively low temperatures to allow for the reduction of nickel oxide to metallic nickel in a gentle way. The hydrogen does not impact the stability of the cathode if the fuel cell sealing is perfect, however, for the SC-SOFCs, because both electrodes are located in the single-gas chamber, the *in situ* reduction of the anode with highly reducing hydrogen gas also results in the reduction of the cathode [14]. Previously, we proposed the *ex situ* reduction of NiO to Ni before depositing the cathode layer over the anode/electrolyte half-cell [15]. To avoid the re-oxidation of metallic Ni to NiO, calcination of the cathode layer should be performed in an inert atmosphere to establish sufficient mechanical strength. The need for a controlled atmosphere inevitably increases the complexity of cell fabrication and, thus, the capital cost, making SC-SOFCs less attractive for practical applications. Additionally, the use of an organic additive in the cathode precursor, which is added to prepare a proper slurry for painting onto the electrolyte surface, could create a local reducing atmosphere around the cathode during firing in inert atmosphere. Thereby, partial or even deep reduction of the cathode could still result. Thus, it would be preferable for the fuel cells to be *in situ* initialized by the same fuel-oxidant gas mixture for operation in a single-chamber mode.

Recently, we have demonstrated the realization of such *in situ* activation by depositing a Ru–CeO₂ catalyst layer onto the anode surface [16]. The catalyst converted the CH₄–O₂ gas mixture to a highly reducing syngas (H₂ and CO), which diffused into the anode layer to successfully reduce NiO to Ni, while the oxygen partial pressure near the cathode surface was similar to the methane–oxygen gas mixture as a result of the very poor catalytic activity of the cathode toward the partial oxidation of methane; consequently, the phase structure of the cathode material survived during the activation process. However, the Ru–CeO₂ catalyst layer was delaminated from the nickel-based anode after experiencing repeated thermal and redox cycling [17]. Additionally, this layer displayed poor conductivity, introducing additional drawbacks with respect to current collection.

During the past decade, nanostructured materials have received significant attention for their potential application in a wide range

of fields due to their unique properties, which include a large specific surface area, excellent catalytic activity, high adsorption capacity, enhanced cell photochemical inversion rate, etc. [18–21]. Recently, the application of nanostructured materials in SOFCs to improve cell performance has also been exploited, and some progress has been made [22–26]. For example, Zhan et al. reported a SOFC using nanoscale Ni anode prepared by an impregnation method, which exhibited a low anode polarization resistance, as well as significantly improved cell performance measurements [26]. Impregnation is a common method for the introduction of nanoparticles into the porous electrodes of SOFCs.

In this study, we reported that the *in situ* initialization of SC-SOFCs with conventional sintered nickel cermet anode by a methane–oxygen gas mixture was readily realized by modifying the sintered anode with a nanocatalyst, such as RuO₂, CeO₂ or Co₃O₄, which was introduced by a solution impregnation method. The influence of the nanocatalyst on the SC-SOFC initialization process, the cell performance, and the morphological change after the performance test was investigated and is discussed systematically.

2. Experimental

2.1. Cell fabrication

Anode substrates, composed of commercial NiO (Chengdu Shudu Nano-science, China) and (Y₂O₃)_{0.08}(ZrO₂)_{0.92} (YSZ, Tosoh), were prepared using a tape-casting process. To prepare the anode slurry for the tape-casting process, NiO, YSZ, starch (as a pore former) and triethanolamine (as a surfactant) were first ball-mill mixed at the mass ratio of 60:40:10:3 with a mixture of ethanol and dimethylbenzene for 24 h. Second, polyvinyl butyral (as a binder), polyethylene glycol (as a plasticizer) and dibutyl *o*-phthalate (as a plasticizer) with the mass ratio of 14:10:13 were added to the slurry, and then, the slurry was ball milled again for another 24 h. Then, the slurry was cast onto a tape after vacuum pumping to remove the air, and the cast slurry was allowed to dry in air overnight. Finally, the anode substrates were detached from the tape and were then drilled to form disks with diameters of 16 mm. The disks were then calcined at 1100 °C for 2 h to create sufficient mechanical strength. Next, a thin-film YSZ electrolyte layer was deposited onto each anode substrate *via* a wet powder-spraying technique. The anode/electrolyte half-cells were then sintered at 1400 °C for 5 h in air. Finally, a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF) cathode synthesized by using an EDTA-citric acid complexing sol–gel process was sprayed over the central surface of the electrolyte, giving an effective area of 0.48 cm², and each cell was fired at 850 °C for 2 h in air.

The nanocatalyst-modified anode was prepared using a solution impregnation method. A solution of either Ce(NO₃)₃, RuCl₃ or Co(NO₃)₃ was employed as the precursor of CeO₂, RuO₂ or Co₃O₄ nanocatalyst, respectively, at the concentration of 0.5 mol L⁻¹; this solution was impregnated into the unreduced NiO–YSZ anode scaffolds using a manual syringe. For each catalyst, three impregnation steps were performed to ensure sufficient catalyst. The loading of the infiltrated nanocatalysts (CeO₂, RuO₂ or Co₃O₄) was 3 wt.% in the porous NiO–YSZ scaffold. Each impregnation step was followed with a sequence of drying, slow heating to 500 °C at 2 °C min⁻¹ and a dwell time of 30 min in air.

2.2. Activation test

The fuel cell was placed in a single-chamber reactor, and then the CH₄–O₂ gas mixture (CH₄: 200 mL min⁻¹, O₂: 100 mL min⁻¹ [Standard Temperature and Pressure, STP]) was switched on. The

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