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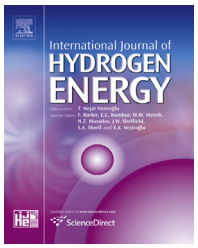

Performance improvement and redox cycling of a micro-tubular solid oxide fuel cell with a porous zirconia support

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ABSTRACT

The performance of a novel micro-tubular solid oxide fuel cell (SOFC) with an inert support and an integrated current collector for the inner electrode was improved by controlling its microstructural features. Multi-step dip coating and co-sintering methods were used to fabricate the cell containing porous yttria-stabilized zirconia (YSZ), Ni, Ni–YSZ, YSZ, strontium-doped lanthanum manganite (LSM)–YSZ, and LSM as the inert support, anode current collector, anode, electrolyte, cathode, and cathode current collector, respectively. To enhance gas diffusion through the YSZ support by properly tailoring its porosity, a combination of micro-crystalline cellulose and polymethyl methacrylate pore formers was used. Additionally, the porosity of the Ni current collector was improved and the LSM–YSZ cathode was sufficiently thick for high oxygen reduction activity. Owing to its optimized microstructure, the micro-tubular SOFC delivered excellent power output with maximum power densities of 710, 591, 445, and 316 mW cm^{-2} at 850, 800, 750, and 700 °C, respectively. The effect of redox cycling on cell performance was investigated by alternately exposing the anode to fuel and air atmospheres. The cell had good tolerance toward the redox phenomenon with no apparent degradation in its performance up to 10 redox cycles.

Introduction

Fuel cells convert the chemical energy in fuels to electric energy with high efficiency and low emissions. They are expected to play an important role in a low-carbon society. Among the different types of fuel cells, solid oxide fuel cells (SOFCs) are known for their ability to use direct hydrocarbon fuels, simplified fuel processing requirement, and cell components with potentially low-cost and abundant materials [1–4]. Additionally, the high-temperature heat produced by SOFCs makes them attractive candidates for combined-cycle and cogeneration plants [5–7]. The thermo-mechanical properties and power generation characteristics of a SOFC are largely influenced by its geometric design. Comparing the two principal SOFC designs (planar and tubular), the tubular design has competitive advantages such as easy sealing and good thermal-cycling behavior [8,9]. In particular, small-diameter tubular SOFCs, commonly known as micro-tubular SOFCs, have received an increasing amount of attention

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because of their high volumetric power densities [10–12]. Because the wall thickness of the cell support can be reduced considerably for small-diameter cells without any compromise in mechanical strength, the micro-tubular design offers further desirable properties that consist of high thermal shock resistance and low thermal mass [10,13]. These properties, in turn, allow for the rapid startup and shutdown of SOFC stacks.

One of the main challenges associated with existing micro-tubular SOFC designs is their poor current collection efficiency from the inner electrode [14–16]. Current can be tapped from the outer electrode by applying current-collecting materials such as wires or meshes over the whole surface. However, these current-collecting materials cannot be applied over the whole surface of the inner electrode because of the small available bore size. Instead, current has to be tapped from the exposed end/s of the inner electrode. This causes a longer current conduction path for the inner electrode, which increases the ohmic resistance. The performance loss because of this kind of ohmic resistance is significant for longer micro-tubular SOFCs with active lengths of more than a few centimeters [14]. To improve the current collection characteristics of micro-tubular SOFCs, we have proposed a novel micro-tubular SOFC design with an integrated current collecting layer for the inner electrode [17,18]. In this design, an inert layer provides structural support to the cell and a thin layer of electrically conducting material on top of the inert layer serves as a current collector for the inner electrode. The thin layer of electrically conducting material can be considered to be identical to a meshed collector with continuous axial contact along the electrode surface, and this is an ideal option for current collection from SOFC electrodes [19]. Simulation studies conducted for micro-tubular SOFCs with an active length of 10 cm have indicated that because of the lower ohmic overpotential, the proposed design can deliver a distinctly better performance compared with the conventional anode-supported designs [18].

Apart from the current collection characteristics, the stability of micro-tubular SOFCs upon undergoing reduction–oxidation (redox) cycles is also of crucial concern. Among state-of-the-art SOFC anodes, Ni–yttria-stabilized zirconia (YSZ) cermet is the most widely used material. It is prepared by mixing NiO and YSZ powders. NiO in the as-prepared anode is reduced to Ni under a fuel atmosphere before power generation. The Ni particles may re-oxidize to NiO during the SOFC operation because of several reasons such as seal deterioration, fuel supply interruption, or very high fuel utilization [20]. Owing to the large difference in molar volumes of the two states of Ni (i.e., 11.198 $cm^3\ mol^{-1}$ for NiO and 6.589 $cm^3\ mol^{-1}$ for Ni), the reduction and oxidation processes, respectively, cause significant shrinkage and expansion of the particles. Because Ni particles do not generally recover to their original states during this redox process, dimensional changes take place in the anode's microstructure [20–23]. These changes give rise to mechanical stresses in the anode as well as the neighboring cell components, which results in the performance degradation of the cell and in the worst case, the structural integrity of the cell may be lost completely [24–26]. In order to improve the redox stability, alternative anode materials such as (La,Sr) $(Cr,Mn)O_3$ [27] and doped $SrTiO_3$ [28,29] have been proposed. However, the performance of these materials in terms of electronic and ionic conductivities, and electrocatalytic activity is still low [30]. Since the Ni–YSZ cermet remains the material of choice for SOFC anodes owing to its electrochemical performance and cost, efforts have been made to improve its dimensional stability under redox conditions via microstructural engineering approaches. One of such approaches is to first prepare a porous YSZ substrate and then introduce Ni particles by infiltration techniques [31–33]. Although the Ni-infiltrated anodes have been found to possess relatively better redox stability, their large-scale production may be time-consuming and costly [34]. On the other hand, the effect of the redox phenomenon is strongly dependent on the type of the cell support. Performance degradation due to redox cycling is more severe for the widely pursued anode-supported designs because dimensional changes in the thick anode layer can easily affect the thin electrolyte layer [20,35]. In contrast, the redox-induced mechanical stresses are expected to be very small for the proposed inert support-based micro-tubular SOFC, which consists of thin anode and anode current collector layers.

In our previous study, a micro-tubular SOFC was successfully fabricated using porous YSZ as the inert support along with Ni, Ni–YSZ, YSZ, strontium-doped lanthanum manganite (LSM)–YSZ, and LSM as the anode current collector, anode, electrolyte, cathode, and cathode current collector, respectively [36]. Although the fabricated cell gave good electrochemical performance, a microstructure optimization of the cell components was found to be imperative for a further improvement in its performance. In this work, gas diffusion through the inert support was enhanced using a combination of micro-crystalline cellulose and polymethyl methacrylate (PMMA) pore formers. The micro-crystalline cellulose has already been shown to provide better shrinkage to the support layer at lower sintering temperatures, whereas PMMA beads result in a macroporous (pore size >50 nm) microstructure with well-defined pores. The macroporous microstructure greatly promotes the transport of the reactant and the product gases [37–39]. Additionally, the porosity of the Ni current collector was improved by increasing the amount of the cellulose pore former from 5 to 10 wt% and the LSM–YSZ cathode was made sufficiently thick for high oxygen reduction activity. The actual effect of redox cycling on the present microtubular SOFC was investigated by alternately supplying humidified H_2 and air to the anode. The change in voltage of a single cell at a

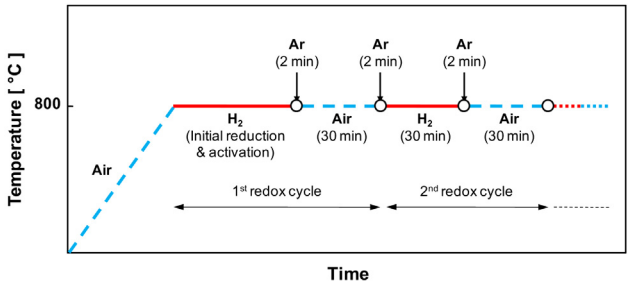

Fig. 1 – Redox cycling protocol showing the alternate supply of H_2 and air to the anode.