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Characteristics of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ -supported micro-tubular solid oxide fuel cells with $\text{LaCo}_{0.4}\text{Ni}_{0.6-x}\text{Cu}_x\text{O}_{3-\delta}$ cathodes

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ARTICLE INFO

Article history:

Received 11 May 2017

Received in revised form

21 January 2018

Accepted 25 January 2018

Available online xxx

Keywords:

Solid oxide fuel cell

Tubular

Extrusion

Dip-coating

Sintering

LSGM

ABSTRACT

In this study, micro-tubular solid oxide fuel cells (T-SOFCs) with extruded $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) electrolyte as the mechanical support and $\text{LaCo}_{0.4}\text{Ni}_{0.6}\text{O}_{3-\delta}$ (LCNO) or $\text{LaCo}_{0.4}\text{Ni}_{0.4}\text{Cu}_{0.2}\text{O}_{3-\delta}$ (LCNCO) as cathodes were prepared and characterized. Partial substitution of Cu for the Ni-ion positions in the LCNO lattices was found to significantly enhance the densification and accelerate the grain growth. The porosity-corrected electrical conductivity was significantly increased from 1275 S/cm for LCNO ceramic to 1537 S/cm for LCNCO ceramic, because the acceptor doping was compensated by the formation of hole carriers that produced additional polarons and significantly augmented the electrical conductivity. SOFCs with three configurations were built in this study, including Cell A that had a lanthanum-doped ceria (LDC) buffer layer inserted between the LSGM electrolyte and the LCNCO cathode, Cell B that used an LCNO-LSGM composite cathode, and Cell C that featured an LCNCO-LSGM composite cathode. Among the three cells, Cell C with 263 μm of LSGM electrolyte possessed the lowest Ohmic resistance of 0.89 $\Omega\text{ cm}^2$, a polarization resistance of 0.69 $\Omega\text{ cm}^2$, and the highest maximum power density of 178 mW cm^{-2} at 750 $^\circ\text{C}$.

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Introduction

Tubular solid oxide fuel cells (SOFCs) exhibit lower thermal stress, easier gas sealing, higher mechanical strength, faster start-up and shut-down times, higher thermal cycling behavior, and more stable performance at high temperatures (700–1000 $^\circ\text{C}$), than planar configurations [1–3]. Processing for tube formation and layer deposition are the key fabrication

steps for tubular SOFCs (T-SOFCs). It has been reported in the literature that forming methods including extrusion, gel casting, isostatic pressing, and phase inversion methods were used to prepare ceramic micro-tubes. Common layer-deposition techniques such as dip-coating, plating, electrophoretic deposition, and spray-coating were developed to lay down the layer structure on the support tube surfaces [4–9]. The lengthy current flow pathways of tubular-type SOFCs increase the internal resistance of the cell and therefore lead to

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<https://doi.org/10.1016/j.ijhydene.2018.01.170>

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a decrease in cell performance [10]. The power density of T-SOFCs is inversely proportional to the tube diameter; thus, micro T-SOFCs provide the advantage of high volumetric power density [6]. Micro T-SOFCs are usually built as either electrolyte-supported or anode-supported designs. Even though a very thin electrolyte layer can be applied on the anode support to increase the Ohmic resistance and improve the cell performance, the electrolyte-supported design is generally regarded to be more stable than its anode-supported counterpart. This is because anode-supported T-SOFCs experience a significant volume change (approximately 40 vol%) in the anode layer during reduction and re-oxidation cycles, which leads to cracking of the thin electrolyte layer and delamination of the electrolyte and electrode layers; hence, this geometry is prone to mechanical failure during operation [7,10].

In previous studies, electrolyte-supported micro T-SOFCs with $Zr_{0.8}Sc_{0.2}O_{2-\delta}$ (ScSZ) or $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC) electrolytes were prepared using extrusion and dip coating [5,11,12]. The micro T-SOFCs with ScSZ electrolyte exhibited good flexural strength (190 MPa), but low maximum power density (MPD)—only about 0.23 W cm^{-2} at 900°C —owing to the high Ohmic and polarization resistances of the cells. On the other hand, the micro T-SOFCs with GDC electrolyte possessed lower Ohmic resistance, and hence could be operated at lower temperature [11,12]. However, they encountered poor mechanical strength and certain level of electronic conduction in the electrolyte, causing a drop in the open-circuit voltage (OCV) [13]. An alternative electrolyte $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) with a perovskite structure was reported to exhibit a superior oxygen ion conductivity five times higher than that of yttria-stabilized zirconia (YSZ) electrolytes (typically 0.17 S cm^{-1} at 800°C and 0.034 S cm^{-1} at 600°C), negligible electronic conduction, and high chemical stability over a broad range of oxygen partial pressures (1×10^{-15} to $1 \times 10^5 \text{ Pa}$), making them a promising electrolyte material for intermediate-temperature SOFCs (IT-SOFCs) [14]. However, it is known that electrode selection is restricted with LSGM because of its reactivity with other nearby components. LSGM reacts with Ni and produces secondary phases of $LaNiO_3$ and La_2NiO_4 , which make the perovskite structure unstable [7]. LSGM reacts with zirconia-based anodes (Ni-YSZ) and ceria-based anodes [Ni-GDC or Ni-samarium doped ceria (SDC)] producing $La_2Zr_2O_7$, $Sr_2Zr_2O_4$, and $SrZrO_3$ phases, and $LaSrGa_3O_7$ and $LaSrGaO_4$, respectively [4,7]. The chemical reaction or ionic migration across the interface introduces either pathways for electronic conduction in the electrolyte or blocking interfacial phases. As reported in the literature on planar SOFC single cells, Yu et al., Bi et al. and Bozza et al. [4,15,16] inserted a $Ce_{0.6}La_{0.4}O_2$ (LDC) layer between an LSGM electrolyte and a NiO anode to prevent the chemical reaction between LSGM and NiO during sintering [17], while Lin et al. and Wan et al. [4,18] introduced LDC between an LSGM electrolyte and both electrodes to improve the cell characteristics. In the literature, there are few reports focusing on dip-coated and electrophoretically deposited LSGM film on tubular anodes [4,19,20]. However, reports of T-SOFCs with LSGM electrolytes as mechanical support for building micro T-SOFCs are rare in the open literature [21,22].

$LaCo_{1-x}Ni_xO_{3-\delta}$ ceramics with $x = 0.4$ or $x = 0.6$ have previously been investigated for use as cathodes for SOFCs,

because of their high electrical conductivity and because their thermal expansion coefficient (TCE) is well matched to other nearby SOFC materials [23]. Up to now, several studies in the literature have investigated the characteristics of SOFCs with $LaCo_{1-x}Ni_xO_{3-\delta}$ cathodes, and only achieved inferior cell performances with a MPD less than 50 mW cm^{-2} [23–26]. This was due to the poor electrochemical performance when using $LaCo_{1-x}Ni_xO_{3-\delta}$ material as a porous SOFC cathode [27]. One possible reason for the low performance of porous single phase $LaCo_{1-x}Ni_xO_{3-\delta}$ cathodes is the fact that $LaCo_{1-x}Ni_xO_{3-\delta}$ requires temperatures above 1000°C to desorb oxygen and create the oxygen vacancies required for materials with considerable oxide ion conductivity.

The goals of the present study were to investigate the electrochemical and cell performances of the T-SOFCs with extruded LSGM electrolyte as mechanical support and $LaCo_{0.4}Ni_{0.6}O_{3-\delta}$ (LCNO)-based ceramic as cathodes. In order to improve the electrochemical performance, two approaches were undertaken: One was to use Cu to partially substitute for the Ni-ion positions in the LCNO lattices, i.e., to use $LaCo_{0.4}Ni_{0.4-x}Cu_xO_{3-\delta}$ (LCNCO) material, while inserting an LDC buffer layer between the LSGM electrolyte and the LCNCO cathode. The phases, microstructures, and electrical conductivities of the LCNO and LCNCO ceramics were examined to clarify the differentiation between the SOFCs with LCNO and LCNCO ceramics as cathodes. The second approach was to mix the LCNO and LCNCO with LSGM to form composite cathodes. The principle idea behind these structures is that the LCNO and LCNCO ceramics provide the electronic conductivity and the LSGM ceramic offers ionic conductivity. All SOFC single cells incorporate a bi-layer anode composed of an LDC-NiO composite layer and a NiO layer. Also, an LDC buffer layer was introduced between the bi-layer anode and the electrolyte to prevent chemical reactions between Ni and LSGM. The electrochemical and cell performances of the micro T-SOFCs with various configurations were evaluated and compared.

Experimental procedure

The cathode powders used in this investigation were synthesized by a solid state reaction method. Highly pure (>99.9% purity) and reagent grade La_2O_3 (Showa), NiO (Alfa), Co_3O_4 (Aldrich), and CuO (Showa) were used as raw materials. Oxides based on the compositions of $LaCo_{0.4}Ni_{0.6}O_{3-\delta}$ (LCNO) and $LaCo_{0.4}Ni_{0.4-x}Cu_xO_{3-\delta}$ (LCNCO) were mixed and milled in a methyl alcohol solution using polyethylene jars and zirconia balls for 24 h and then oven-dried overnight at 80°C . After drying, the powders were calcined at 900°C for 4 h at a heating rate of $5^\circ\text{C} \cdot \text{min}^{-1}$, and then re-milled in methyl alcohol for 24 h. The average particle size and Brunauer-Emmett-Teller (BET) surface area of the calcined LCNO and LCNCO powders were determined using a laser-scattering particle-size distribution analyzer (Horiba LB-500) and a surface area and porosity analyzer (Micromeritics ASAP2020), respectively. Phase identification on the calcined powders was conducted using X-ray diffraction (XRD, Rigaku DMAX-2200) with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). For measuring electrical conductivity, the powders were added to 5 wt% of a 15%-polyvinyl acetate

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