



Electrochemical performance and stability of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ and $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ - $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ anode with anode interlayer in H_2 and CH_4



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ABSTRACT

Donor-doped SrTiO_3 is a promising material for use as an alternative anode to solve stability problems due to carbon coking or Ni coarsening etc. of conventional Ni-cermet anodes. Electro-catalytic Ni nanoparticles can be produced in La and Ni co-doped SrTiO_3 or $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (LSTN) anode when it is exposed to a reducing atmosphere. In this work, we study the effects of $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (GDC) either as an anode interlayer (between anode and electrolyte) or as a composite phase in an anode composed of La and Ni co-doped SrTiO_3 ($\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$, LSTN). The electrochemical performance (i.e., impedance spectra and power density) of electrolyte-supported cells in which scandia-stabilized zirconia (ScSZ) is used as an electrolyte and LSTN or LSTN-GDC is used as the anode, are examined and compared at 800°C in H_2 and CH_4 fuels. LSTN anode was stable and had improved performance in both H_2 and CH_4 fuels when GDC was composited and also used as an anode interlayer. A significant reduction of anodic polarization resistance in CH_4 gas is clearly demonstrated.

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1. Introduction

Solid oxide fuel cells (SOFCs) are highly efficient, ecologically benign energy generation devices that can use a various fuels [1]. Stability of SOFCs is one of main requirements for SOFC systems. The stability of the anode is one of the most important determinants of its performance. Conventional Ni-cermet anodes have many demerits such as poor redox stability, Ni coarsening, carbon deposition when used with hydrocarbon fuels, and poisoning by sulfur in fuels [2–4]. Stability of the anode is a main requirement for SOFC systems, so improvement of SOFCs requires development of alternative anode materials.

Many efforts have been made to develop new anode materials, e.g., Cu– CeO_2 , Ru– CeO_2 [5–7]. Perovskite oxides such as strontium or manganese doped LaCrO_3 [8], donor-doped SrTiO_3 [9–11] are good candidates as alternative anode materials for SOFCs because these compounds can use methane gas (CH_4) as fuel without reforming, and because they are sulfur-tolerant [12]. However, their impedance spectra and power density (“electrochemical performance”) are not satisfactory. Power density can be increased

or polarization resistance can be decreased by impregnating the anode with Ni or Pd particles [9,13], but this method involves repeated infiltration of solution and firing, so it has demerits including process complexity and inhomogeneous distribution of catalyst particles.

A relatively simple ex-solution process generates electro-catalytic nanoparticles by incorporation and ex-solution of Ni, Co, Cu, Pd, or Ru in perovskite oxides [10,14–16]. Strontium titanate doped with a donor (e.g., lanthanum, yttrium) is attractive as an alternative anode, so $\text{La}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (LST) and $\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (LSTN) have been evaluated as anode candidates [10,17]. The solubility of Ni in LST after calcination in air at 1300°C is limited to $\sim 10\text{ mol}\%$. The degrees of Ni ex-solution and Ti reduction depend on time and temperature of heat-treatment in reducing H_2 atmosphere. Ni ex-solution reaction is faster than Ti reduction. The temperature and atmosphere (air, H_2) of LSTN anode firing is critical to control the degree of Ni ex-solution, and the microstructure and electrochemical performance of an LSTN anode.

The LST or LSTN should be good electronic conductors because they contribute negligibly to the Ohmic resistance R_Ω of the anode in the cell. The electrical (or electronic) conductivity σ of donor-doped SrTiO_3 varies widely depending upon its thermodynamic (temperature and atmosphere) history due to its slow equilibrium

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kinetics [18,19]; therefore conductivity is difficult to define if the sample size and thermodynamic condition are not specified. For pellet form of $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$, e.g., σ at 1000°C is much higher in H_2 ($\sim 100\text{ S}\cdot\text{cm}^{-1}$) than in air ($\sim 10^{-2}\text{ S}\cdot\text{cm}^{-1}$); this difference has been explained by a proposed defect model [20].

With additional Ni doping, similar tendency was shown. $\text{La}_{0.5}\text{Sr}_{0.5}\text{Ti}_{0.75}\text{Ni}_{0.25}\text{O}_{3-\delta}$ in air at 800°C has $\sigma \sim 0.002\text{ S}\cdot\text{cm}^{-1}$, but a pre-reduced sample in humidified Ar/H_2 (98/2) at 800°C had $\sigma \sim 2\text{ S}\cdot\text{cm}^{-1}$ [18]. σ of the composite phase is generally similar to σ of the most conductive phase in the composite, e.g., for pre-reduced and dense $\text{SrTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}$ - CeO_2 composite in humidified H_2 at 800°C , σ was $\sim 4\text{ S}\cdot\text{cm}^{-1}$ [21]. A porous sample has poor connectivity, so it has much lower σ than does a dense sample. Porous $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ - YSZ composite in wet H_2 (3% H_2O) at 800°C has $\sigma \sim 0.05\text{ S}\cdot\text{cm}^{-1}$ [22]. The conductivity of donor-doped SrTiO_3 may also be stable or change with time depending upon temperature when exposed to anode atmosphere due to its equilibrium kinetics [23–25].

Although LST and LSTN are promising as anode materials, they react with the zirconia electrolyte and form secondary phases such as insulating $\text{La}_2\text{Zr}_2\text{O}_7$ (LZO)/ SrZrO_3 [26,27] similar to the reaction between $(\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3$ and Y_2O_3 (3 or 8 mol%)-doped ZrO_2 [28,29]. In addition, Ti in LSTN may react with the zirconia electrolyte during high-temperature fabrication. Because the solubility of TiO_2 in YSZ is significant (10–15 mol%) [30–34], diffusion of Ti into YSZ may induce significant electronic conductivity and consequent decrease in the performance of a cell. The ionic transport number of 10 mol% TiO_2 -doped YSZ sintered at 1500°C in air is 0.78 at 1000°C [31]. Thus, to ensure the stability of LST or LSTN anodes in SOFCs an anode interlayer must be introduced; this layer must both block the formation of an insulating layer and prevent the introduction of electronic conductivity.

Therefore, in this study, an anode interlayer with $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (GDC) composition was introduced between anode and electrolyte to block the interfacial reaction between La and Ti of the LSTN anode and Zr and Sc of the ScSZ electrolyte. The use of GDC interlayer between La-containing cathode and zirconia-based electrolyte is well established [35–38].

Reaction between GDC and ScSZ is also expected; it may be similar to the well-known reaction between GDC and yttria-stabilized zirconia (YSZ) [39–41]. Inter-diffusion of Ce and Zr between GDC and YSZ forms a solid-solution phase that has lower σ than either YSZ or GDC [35,36]. Further study may be needed to confirm the reaction between ScSZ and GDC, however, the reaction may be similar to that of YSZ and GDC because in both cases the main diffusing elements are Ce and Zr.

The effect of the anode interlayer on the performance of SOFC was investigated. In addition, donor-doped SrTiO_3 has poor ionic conductivity [42], so to improve the anodic performance, GDC was mixed or composited with LSTN to provide an ionic conduction path. The mixing ratio of LSTN and GDC was fixed to 3:7 (wt:wt), following the results of previous work [43]. No other phase was observed in LSTN-GDC composite after usual firing [9].

Conventional Ni-GDC cermet anode was used as a reference for comparison with LSTN-GDC composite anode. The electrolyte-supported cell with scandium-stabilized zirconia (ScSZ) as an electrolyte was used to measure the impedance spectra and power density of the cell in H_2 and CH_4 fuels.

2. Experimental

$[\text{Sc}_2\text{O}_3]_{0.1}[\text{CeO}_2]_{0.01}[\text{ZrO}_2]_{0.89}$ (ScSZ or 10Sc1CeSZ, Fuel Cell Materials, USA) as a self-supported electrolyte ($\sim 300\ \mu\text{m}$ thick, $\sim 18\text{ mm}$ diameter) was prepared using tape casting, then sintered at 1400°C for 5 h in air. LSTN and GDC powders were prepared using solid-state reaction. The raw oxides for LSTN and GDC were calcined at 1300°C for 10 h in air and for 1150°C for 2 h in air, respectively. The calcined LSTN and GDC powders were planetary milled (Pulverisette 6, Netzsch, Germany) for 4 h with zirconia balls and ethanol.

$\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (GDC) was used as an interlayer to prevent an interface reaction between the cathode and electrolyte or between the anode and electrolyte. The GDC paste for either cathode (for all samples) or anode interlayer (for select samples) was screen-printed onto the sintered ScSZ electrolyte and heated at 1400°C for 5 h in air. Detailed information on preparation of LSTN and GDC powders, ScSZ tape, GDC pastes can be found elsewhere [10,17]. The thickness of GDC interlayer was $\sim 2\ \mu\text{m}$ after firing. LSTN and GDC powders were mixed in 3:7 (wt:wt) ratio by planetary milling for 4 h to produce composite powder for the anode. The pastes for LSTN and LSTN-GDC anodes for screen printing were prepared by a method similar to that used to prepare GDC paste. NiO and GDC powders were mixed in 6:4 (wt:wt) ratio by planetary milling for 4 h to produce composite powder for anode. NiO-GDC paste was also similarly prepared for comparison.

Table 1 shows sample descriptions for LSTN-based anode materials with the same firing condition. Ni-GDC added as a comparison does not use anode interlayer and use a different firing condition. LSTN and LSTN-GDC pastes were screen-printed on top of the GDC interlayer which was pre-coated on ScSZ electrolyte. LSTN and LSTN-GDC anodes were fired in H_2 at 1250°C for 2 h after screen printing on ScSZ electrolyte layer. NiO-GDC anodes were screen-printed on top of the sintered ScSZ electrolyte pellet without using a GDC interlayer. Ni-GDC anode was fired in air at 1100°C for 2 h after screen printing. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ - $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_2$ (LSCF-GDC, Fuel Cell Materials) composite was used as a cathode for all samples. After firing anode at 1250°C for 2 h in wet H_2 (97% H_2 + 3% H_2O), the cathode paste was screen-printed on top of the GDC interlayer and fired at 1040°C for 2 h in air. During cathode firing of cells in air, the Ni particles ex-soluted from LSTN-based anodes during anode firing were only slightly re-dissolved in LSTN lattice [17]. Thus the cathode firing process has little effect on anode performance.

The coating and firing steps are summarized for clarity. For the cells with LSTN and LSTN-GDC anodes, GDC layers were coated as both anode and cathode interlayers and thus both on cathode and anode side of ScSZ electrolyte. For the cell with Ni-GDC anode, GDC

Table 1
Composition and firing condition (temperature and atmosphere) of anode materials. GDC was used as an anode interlayer between electrolyte and LSTN or LSTN-GDC composite anodes. For the ScSZ-electrolyte supported cell, screen-printed LSCF-GDC (5:5 wt:wt) cathodes were fired at 1040°C for 2 h in air for all samples. GDC was also screen-printed as an interlayer between the cathode and the ScSZ electrolyte in all samples. Wet H_2 indicates 97% H_2 + 3% H_2O .

Sample notation	Anode composition	Anode firing	Remark
LSTN	$\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_3$	$1250^\circ\text{C}/\text{wet H}_2$	With GDC Anode interlayer
LSTN-GDC	$\text{La}_{0.2}\text{Sr}_{0.8}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_3$ - $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_2$ (3:7 wt:wt)	$1250^\circ\text{C}/\text{wet H}_2$	With GDC Anode interlayer
Ni-GDC	NiO - $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_2$ (6:4 wt:wt)	$1100^\circ\text{C}/\text{Air}$	No anode interlayer

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