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$La_2NiO_{4+\delta}$ potential cathode material on $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ electrolyte for intermediate temperature solid oxide fuel cell

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ABSTRACT

$La_2NiO_{4+\delta}$, a mixed ionic-electronic conducting oxide with K_2NiF_4 type structure, has been studied as cathode material with $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM) electrolyte for intermediate solid oxide fuel cells (IT-SOFCs). XRD results reveal excellent chemical compatibility between the $La_2NiO_{4+\delta}$ sample and LSGM electrolyte.

A single cell (0.22 cm^2 active area) was fabricated with $La_2NiO_{4+\delta}$ as cathode, Ni–$Sm_{0.2}Ce_{0.8}O_{1.9}$ (2:1; w/w) as anode and LSGM as electrolyte. A thin buffer layer of $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) between anode and electrolyte was used to avoid possible interfacial reactions. The cell was tested under humidified H_2 and stationary air as fuel and oxidant, respectively. The electrochemical behaviour was evaluated by means of current–voltage curves and impedance spectroscopy. Microstructure and morphology of the cell components were analysed by SEM-EDX after testing.

The maximum power densities were 160, 226, and 322 mW cm^{-2} at 750, 800 and 850 °C, respectively with total polarisation resistances of 0.77, 0.48 and 0.31 $\Omega\,cm^2$ at these temperatures. Cell performance remained stable when a current density of 448 mA cm^{-2} was demanded for 144 h at 800 °C, causing no apparent degradation in the cell. The performance of this material may be further improved by reducing the electrolyte thickness and optimisation of the electrode microstructure.

1. Introduction

Solid oxide fuel cell (SOFC) is one of the most promising highly efficient energy-conversion systems. Currently, one of the critical targets for the commercialization of SOFC devices is to reduce the operation temperature, from above 900 °C to an intermediate temperature range (600–800 °C). However, there are two notable technical challenges in intermediate temperature solid oxide fuel cell (IT-SOFC) development; one is the lower ionic conductivity of the electrolyte and the other is the lower electrochemical activity of electrodes at reduced temperatures [1].

The increase of ohmic loss due to the lower ionic conductivity of the electrolyte may be minimised by using high ionic-conducting materials such as doped ceria, doped lanthanum gallate or scandia-stabilised zirconia. Among these electrolyte materials, Sr and Mg co-doped lanthanum gallate-based electrolytes (LSGM) are most interesting for IT-SOFC, because LSGM exhibits a conductivity several times higher than 8 mol% yttria-stabilised zirconia (YSZ) at temperatures of 650–800 °C [2], comparable to that of gadolinium doped CeO_2, and an ionic transport number close to unity within large ranges of oxygen partial pressure and temperature [3,4]. However, LSGM is known to have higher chemical reactivity with Ni-based cermet anodes [5,6]. The reactivity between LSGM and Ni results in the formation of high-resistivity compounds at the interface such as $LaNiO_3$ and $LaSrGa_3O_7$. These reaction products would lead to the degradation of cell performance because of an anomalous increase in ohmic loss. Some inert buffer layers of $Ce_{0.6}La_{0.4}O_2$ (LDC), $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC) or $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) have been proposed to avoid the formation of undesirable compounds [5–9]. Thus, Yan et al. [9] reported that the incorporation of an interlayer of SDC (400 nm thick) between the anode of NiO–Fe_2O_3–SDC and the LSGM electrolyte avoids the reaction between LSGM and NiO and also promotes the electrode processes.

The polarisation loss of a cell also greatly increases at low temperature, mainly due to the large cathode overpotential. In order to solve this problem, mixed ionic and electronic conducting (MIEC) materials have attracted much attention as potential cathodes for IT-SOFC. It is believed that the improved electrode properties are due to the extended reaction sites from the three phase boundary region (TPB) to the whole electrode surface, consequently the cathode polarisation obviously decreases and enhances the cell performance at reduced temperatures when a MIEC is used as cath-

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ode [10,11]. Most studies concerning MIEC cathode materials deal with perovskite-type oxides [12–18]. In the last decade, a new family of compounds formulated $A_2MO_{4+\delta}$ with the K_2NiF_4-type structure has received much attention as potential cathode materials for IT-SOFC [19–25]. Among the most studied are the pure and doped $La_2NiO_{4+\delta}$ because of their ability to accommodate a large oxygen overstoichiometry. These compounds exhibit a relativity high oxygen-ion diffusivity, thermal expansion coefficients (TECs) compatible with solid electrolytes, predominant p-type electronic conductivity in the whole $p(O_2)$ range where the K_2NiF_4-type phases exist, and high electrocatalytic activity [26,27]. Previous studies performed by our group revealed that the $La_2NiO_{4+\delta}$ compound presents an oxygen excess (δ) of 0.17 [28] and exhibits relatively high electrical conductivity, thermal expansion coefficient compatible with yttrium-stabilised zirconia (YSZ) and Sr and Mg co-doped lanthanum gallate (LSGM) electrolytes as well as good electrocatalytic activity for the oxygen reduction on LSGM at intermediate temperatures [29,30].

In this study, the $La_2NiO_{4+\delta}$ compound has been investigated as a cathode material for application in IT-SOFC based on a LSGM electrolyte. The chemical compatibility between $La_2NiO_{4+\delta}$ and LSGM was analysed by X-ray diffraction (XRD). Electrochemical measurements have been performed in single cell to evaluate performance and stability. Post test analyses of cell components have been carried out with a scanning electron microscope and energy-dispersive X-ray spectroscopy (SEM–EDX) in order to study the microstructure and morphology.

2. Experimental

$La_2NiO_{4+\delta}$ powder was synthesised via a nitrate–citrate route as cathode material. Stoichiometric amounts of analytical grade La_2O_3 (98.5%) and $Ni(NO_3)_2{\cdot}6H_2O$ (99%) (Panreac) were dissolved in nitric acid (65%) (Merck). Citric acid (99.5%) (Panreac) was added in a large excess (3.3 moles per mole of nickel nitrate) under continuous stirring. The solution was dehydrated and slowly heated until self-combustion of the precipitate. Precursors obtained by the means were calcined at 600 °C for 2 h and finally fired in air at 950 °C for 8 h [29]. The sample was characterised by X-ray diffraction (XRD) for phase identification and phase purity assesment. XRD analysis was performed with a Philips “X Pert-MPD” diffractometer using Cu K_α radiation (λ = 1.5406 Å). The diffraction patterns were recorded in the 20°–80° 2θ range with a scan step of 0.04°. Chemical compatibility of the $La_2NiO_{4+\delta}$ oxide with the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) electrolyte (Praxair) was investigated by mixing the cathode material and electrolyte powders in a 1:1 weight ratio, following by calcination at 1000 °C for 50 h. The resulting mixture was analysed by XRD.

The electrolyte pellet was prepared by uniaxial pressure and calcination at 1500 °C for 10 h from the powder electrolyte. The surface of the electrolyte was roughened by mechanical grinding to reduce its thickness. After sintering, a dense LSGM pellet was obtained with a diameter of ~11 mm and a thickness of ~0.4 mm.

Nickel oxide (NiO, Panreac) and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC, Praxair) were used to prepare the NiO–SDC composite as an anode material. The anode ink was prepared by mixing the powders of NiO and SDC (66.7:33.3 wt.%) in an agate mortar milled with acetone and left to dry in air. After that, a binder (Decoflux, WB41, Zschimmer and Schwartz) was added to obtain a slurry. To prevent the reaction between Ni-SDC and LSGM, a SDC buffer layer was first prepared by painting onto the anode side of the LSGM electrolyte. After heating the buffer layer at 1100 °C for 4 h, the anode ink was painted onto the SDC layer and heated at 1100 °C for 4 h.

The cathode ink was prepared following the same procedure with the $La_2NiO_{4+\delta}$ compound as the material. The cathode ink was deposited on the other side of the electrolyte by painting. After that, the cell was fired at 1000 °C for 4 h with a ramp rate of 2 °C min^{-1}. Finally, Au current collector and Pt current collector was placed on the anode and cathode using Au and Pt inks, respectively, and fired at 900 °C for 2 h. During initial heating, humidified hydrogen (3% H_2O) was supplied in order to reduce the anode NiO–SDC to Ni–SDC cermet.

Cell performance was evaluated using an in-house built test station. The single cell, with an active area of 0.22 cm^2, was sealed into an alumina tube with a ceramic cement (Aremco, Cerambond 525). Humidified hydrogen (3% H_2O) with a flow rate of 50 ml min^{-1} was fed to the anode chamber, while the cathode was simply exposed to air. Electrochemical measurements were conducted using AUTOLAB system (PGSTAT30 and FRA2 module) from Eco Chemie. The current–voltage (I–V) characteristic of the cell was measured using linear sweep voltammetry at a scan rate of 10 mV s^{-1}. The impedance of the cell was recorded at open circuit in galvanostatic mode in a frequency range from 0.1 Hz to 1 MHz and excitation signal of 5 mA.

Microstructure and morphology of the cell and its components were analysed by a scanning electron microscopy (SEM, Hitachi S-2500), equipped with an X-ray analyzer for energy dispersive X-ray (EDX) spectroscopy.

3. Results

XRD patterns of the $La_2NiO_{4+\delta}$ –LSGM mixture calcined at 1000 °C for 50 h are shown in Fig. 1. For comparison, the pattern of the $La_2NiO_{4+\delta}$ and LSGM powders are displayed in the same figure. $La_2NiO_{4+\delta}$ oxide presents a single phase K_2NiF_4-type structure, and no impurities were observed (Fig. 1b). In a previous article [31], we determined its structure from neutron powder diffraction data in the orthorhombic $Fmmm$ space group, with unit cell parameters a = 5.4629 Å, b = 5.4612 Å, c = 12.7039 Å and V = 379.01 Å^3 [28]. LSGM powders exhibit single phase perovskite

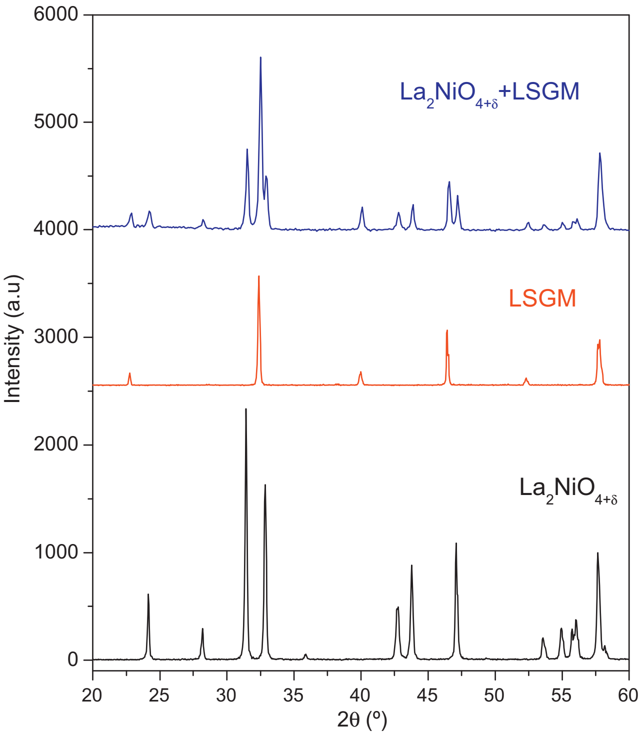

Fig. 1. XRD patterns of $La_2NiO_{4+\delta}$ powders, LSGM powders and the $La_2NiO_{4+\delta}$ –LSGM mixture calcined at 1000 °C for 50 h.