



A new anode material for solid oxide electrolyser: The neodymium nickelate $\text{Nd}_2\text{NiO}_{4+\delta}$

F. Chauveau^a, J. Mougin^b, J.M. Bassat^a, F. Mauvy^a, J.C. Grenier^{a,*}

^a CNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr. A. Schweitzer, Pessac, F-33608, France

^b CEA-Grenoble, LITEN/DTH, 17 rue des Martyrs, F-38054 Grenoble Cedex 9, France

ARTICLE INFO

Article history:

Received 30 April 2009

Received in revised form 29 July 2009

Accepted 3 August 2009

Available online 12 August 2009

Keywords:

Solid oxide electrolysis cell (SOEC)

High temperature steam electrolysis (HTSE)

Anode material

Oxygen electrode

Nickelate oxide

Impedance spectroscopy

ABSTRACT

Neodymium nickelate, with composition $\text{Nd}_2\text{NiO}_{4+\delta}$ is integrated as oxygen electrode in a solid oxide electrolyte supported cell made of a TZ3Y electrolyte and a Ni-CGO hydrogen electrode. This cell is tested in both fuel cell (SOFC) and electrolysis (SOEC) mode and the reversible operation is proven, ASR values being slightly lower in electrolysis mode. Performances in SOEC mode are compared with a commercial cell based on the same electrolyte and cathode, but with lanthanum strontium manganite (LSM) as anode. For a voltage of 1.3 V, current densities of 0.40, 0.64 and 0.87 A cm^{-2} are measured at 750, 800 and 850 °C, respectively; they are much higher than the ones measured in the same conditions for the LSM-containing cell. Indeed, for a voltage of 1.3 V, current densities are respectively 1.7, 3 and 4.2 times higher for the $\text{Nd}_2\text{NiO}_{4+\delta}$ cell than for the LSM one at 850, 800 and 750 °C, respectively. Consequently, $\text{Nd}_2\text{NiO}_{4+\delta}$ can be considered as a good candidate for operating below 800 °C as oxygen electrode for high temperature steam electrolysis.

© 2009 Published by Elsevier B.V.

1. Introduction

For economical and ecological reasons, hydrogen is considered as a major energetic vector for the future. In order to gain the status of leading alternative fuel, one major question which still remains to be solved, is the massive production using clean processes with low or no CO_2 emissions. High temperature steam electrolysis (HTSE) is one of the most promising processes to achieve this target, water molecule being split into hydrogen and oxygen using electricity and heat which can be provided by nuclear power plants for example [1]. However, in order to produce by HTSE the amount of hydrogen needed to replace even partially the fossil fuels, many dedicated power plants would be necessary. Thus, the development of highly efficient systems is required. Each component of the system has to be optimized, from the balance of plant to the solid oxide electrolysis cell (SOEC) where the HTSE reaction occurs. Most of current studies reported on HTSE consider reversible solid oxide cells (fuel cell/electrolysis cell) [2–5], containing hydrogen electrode made of cermet, zirconia based electrolyte, and perovskite-type oxygen electrode. An alternative oxygen electrode material, whose composition is $\text{Nd}_2\text{NiO}_{4+\delta}$, is presented in this work.

The $\text{Ln}_2\text{NiO}_{4+\delta}$ -type oxides (with the K_2NiF_4 -type structure) have been selected because of their aptitude to accommodate a large oxygen overstoichiometry, especially under oxidizing conditions [6], this capability leading to a mixed electronic and ionic conductivity of these materials. This explains the strong interest in these compounds as solid oxide fuel cell (SOFC) cathode material [7]. Recently it was reported that, under anodic polarization, $\text{La}_2\text{NiO}_{4+\delta}$ oxide exhibits a lower polarization resistance than under cathodic polarization [8]. The $\text{Nd}_2\text{NiO}_{4+\delta}$ oxide was selected for this study because of its higher overstoichiometry compared to the other $\text{Ln}_2\text{NiO}_{4+\delta}$ -type oxides [9], which should lead to further improved performances.

Results on performances of this material in SOEC mode are reported here in comparison with the classical LSM (lanthanum strontium manganite) perovskite oxygen electrode. Polarization (i - V) curves are presented at different temperatures on single cells and discussed in combination with corresponding electrochemical impedance spectroscopy (EIS) measurements. Thanks to the use of a specific setup containing a reference electrode, anodic and cathodic contributions are separated and discussed.

2. Experimental

2.1. Description of the cell

The single solid oxide cell (SOC) concerned with this work is a planar electrolyte supported cell. The electrolyte has a 50 mm

* Corresponding author. Tel.: +33 5 40 00 62 62; fax: +33 5 40 00 27 61.
E-mail address: grenier@icmcb-bordeaux.cnrs.fr (J.C. Grenier).

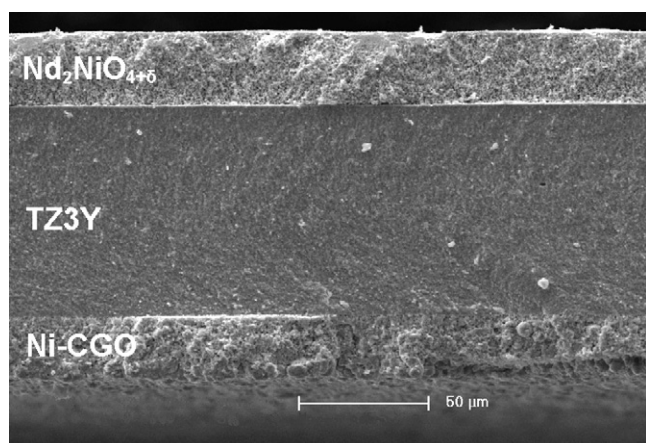


Fig. 1. SEM micrograph of the cell cross-section after electrochemical measurements.

diameter and both electrodes have a 20 mm diameter, which corresponds to a 3.14 cm² active surface area. The oxygen electrode (Nd₂NiO_{4+δ}) was manufactured at ICMCB and deposited on half cells composed of electrolyte and hydrogen electrode provided by H.C. Starck Ceramics GmbH & Co. KG [10].

The electrolyte is a 90 μm thick substrate of 3% tetragonal yttria stabilized zirconia (TZ3Y) and the hydrogen electrode is a 30 μm thick porous nickel and gadolinia doped ceria cermet (Ni-CGO).

The Nd₂NiO_{4+δ} powder was prepared by the nitrate–citrate route as described by Courty et al. [11]. Stoichiometric amounts of neodymium and nickel oxides were dissolved in diluted nitric acid. After addition of a large excess of citric acid for chelating the cations, the solution was dehydrated and heated until self-combustion of the precipitate to obtain submicronic precursor particles [9]. The final annealing was performed at 1000 °C for 12 h to obtain a single phase. The powder was then ball milled to obtain a median grain size ($d_{0.5}$) of about 0.8 μm. A terpeneol-based slurry was prepared with this powder, and then deposited on the electrolyte by screen printing before a sintering step at 1100 °C for 3 h in air [12]. The thickness of the final Nd₂NiO_{4+δ} porous layer was about 30 μm (Fig. 1).

A gold annular reference electrode (2 mm wide) was painted on the oxygen electrode side of the electrolyte and then annealed at 750 °C for 30 min in air (Fig. 2). The distance between working and reference electrodes (more than 100 times the thickness of the electrolyte) was set to avoid as much as possible measurement artifacts due to the influence of the current lines through the electrolyte on the reference electrode [13]. The studied cell was placed in a ceramic housing and sealed using glass paste and gold rings, the whole being inside a specific setup equipped with a so-called 3rd chamber with controlled atmosphere for the reference electrode (Fig. 2). The pressure in each chamber was 1 atm. Before

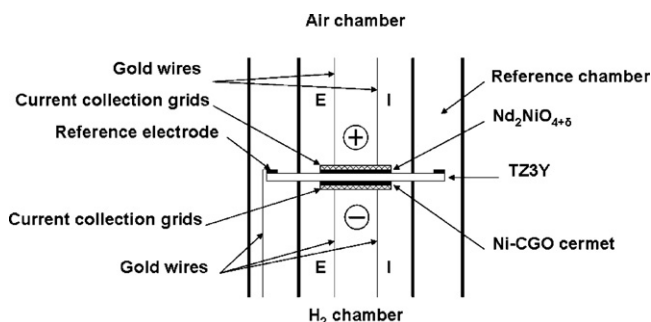


Fig. 2. Schematic representation of the test rig.

electrochemical measurements, the hydrogen electrode provided under NiO-CGO form was reduced at 750 °C in an Ar/H₂ mixture with increasing amounts of hydrogen, up to 100%.

With the aim of comparing, a commercial electrolyte supported cell provided by H.C. Starck Ceramics GmbH & Co. KG under the commercial name ESC2 was also tested in the same conditions. Electrolyte and hydrogen electrode were identical as described above, while the oxygen electrode was a double layer made of pure LSM and 8YSZ (8% yttria stabilized zirconia)/LSM, with a total thickness around 30–50 μm.

2.2. Electrochemical measurements

The inlet gas composition at the hydrogen electrode was composed of hydrogen (4 L h⁻¹), water vapor (3.7 L h⁻¹) and argon (3 L h⁻¹). This amount of water vapor was obtained by total evaporation of liquid water (3 mL h⁻¹). All the measurements reported hereafter were recorded for a ratio $p(\text{H}_2\text{O})/p(\text{H}_2)=0.9$. The inlet gas to the Nd₂NiO_{4+δ} side was air (7 L h⁻¹), the reference electrode compartment was under an argon flow in order to fix a constant oxygen partial pressure at the reference electrode. Current collectors on both positive and negative electrodes were gold grids (1024 meshes cm⁻²) and platinum grids (3600 meshes cm⁻²), platinum grid being directly in contact to the electrodes. This assembly aims to get a good contact with ceramic electrodes. Measurements were performed at 750 °C, 800 °C and 850 °C, from the lowest to the highest temperature. *i*-*V* curves were recorded first in SOFC mode, then in SOEC mode. Measurements were recorded from open circuit cell voltage (OCV) to the highest polarization, then back to OCV.

The current–voltage curves were obtained by applying a dc current during 180 s for each step and recording the voltage after stabilization. These data were recorded using a power supplier (TTi QL355P 15V-5A) under galvanostatic control. The EIS measurements were also performed under galvanostatic control with a 100 mA modulation amplitude, from 10⁴ to 10⁻¹ Hz, using an Autolab PGSTAT 302N equipped with a frequency response analyzer (FRA).

The ratio of steam-to-hydrogen conversion is calculated as the molar amount of hydrogen produced (according to the Faraday's law and assuming 100% of current efficiency) divided by the molar amount of water in the inlet cathodic gas. Cell performances are evaluated through the area specific resistance (ASR) values determined at 0.7 V in SOFC mode and at 1.3 V in SOEC mode. ASRs are calculated as the slopes of *i*-*V* curves between 0.65 and 0.75 V for SOFC mode, and between 1.25 and 1.35 V in SOEC mode.

i-*V* curves and impedance diagrams were recorded on complete cell on one hand (between anode and cathode), and on the other hand using the reference electrode, that is to say between anode and reference or between cathode and reference to separate the anode and cathode contributions to the global signal.

3. Results and discussion

3.1. Cell performances

Current–voltage curves given in Fig. 3, for the three temperatures, were recorded first in fuel cell mode, then in electrolysis one, starting from OCV in each case. These results show that cell can be operated both in SOFC and SOEC modes in agreement with previous studies [2,4]. One should note that the measured OCVs are somewhat smaller than the theoretical Nernst potentials, typically at 800 °C, 0.86 V instead of 0.95 V, which reflects the presence of a slight leak in the setup.

Plots in fuel cell mode are quite linear, highlighting the absence of activation. In electrolysis mode, curves are inflecting, likely reflecting an activation phenomenon. No limiting current

Download English Version:

<https://daneshyari.com/en/article/1289306>

Download Persian Version:

<https://daneshyari.com/article/1289306>

[Daneshyari.com](https://daneshyari.com)