



Electricity/hydrogen conversion by the means of a protonic ceramic electrolysis cell with $\text{Nd}_2\text{NiO}_{4+\delta}$ -based oxygen electrode

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ABSTRACT

The efficient conversion of electrical energy to chemical energy poses new fundamental challenges in the fields of technology, economy and ecology. Currently, development of steam electrolysis technology via solid oxide electrolysis cells (SOECs) is considered to be one of the most effective ways to produce hydrogen. Here, we present testing of the SOEC based on a new combination of the functional materials, $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ as a proton-conducting electrolyte and $\text{Nd}_{1.95}\text{Ba}_{0.05}\text{NiO}_{4+\delta}$ (NBN) as an oxygen electrode, which are chemically and thermally compatible. To demonstrate the performance capability and establish the most favorable operating conditions, the cell was comprehensively characterized within a wide range of temperatures (500–750 °C), applied electrolysis potentials (~0.8–2 V) and water vapor partial pressure in anode atmospheres (0.03–0.5 atm). The results reveal that a high current density 1.21 A cm^{-2} is achieved under the selected conditions (750 °C, 1.6 V, 0.03 atm); it increases up to 1.40 A cm^{-2} with the pH_2O increasing from 0.03 to 0.5 atm. Comparative analysis presented for similar SOEC systems allows considering the NBN as a highly attractive oxygen electrode, having a polarization resistance (R_p) of $0.05 \Omega \text{ cm}^2$ at the selected conditions and promoting electrochemical steam electrolysis because no degradation of the R_p value ($0.03 \Omega \text{ cm}^2$) at highly moisturizing conditions, $\text{pH}_2\text{O} = 0.50 \text{ atm}$.

1. Introduction

Solid oxide electrolysis cells (SOECs) have attracted worldwide attention as prospective hydrogen and synthetic fuel generation devices due to a number of advantages over conventional electrolyzers, such as high electrical-to-chemical energy conversion efficiency, lower energy consumption, environmentally friendly operation and reliability [1–4]. SOECs operate in the reverse mode of solid oxide fuel cells (SOFCs) and, therefore, consist of the same functional materials typically employed in SOFCs [5–7]. For all the mentioned electrochemical solid oxide cells, the requirement to reduce the operating temperatures (below to 800 °C) is a current issue. Solving this problem will eliminate their degradation process, extend their life-time, reduce manufacturing costs and ultimately identify the optimal strategy for their commercialization [8–10].

Investigations relating to material issues and different technological aspects have recently been conducted in attempts to overcome this challenge [5–10]. One of them includes employing proton-conducting oxide electrolytes which demonstrate high ionic (protonic) conductivity with low activation energy [11–13], allowing excellent efficiency and

performance to be achieved at reduced operating temperatures [14–16]. To carry out steam electrolysis in SOECs based on proton-conducting materials (protonic ceramic electrolysis cells, PCECs), the air atmosphere is the source of steam and must necessarily be highly humidified [17]. These conditions are adverse for the functional materials containing alkaline-earth elements due to their possible chemical degradation with the formation of insulating hydroxide phases, especially across the low-temperature region. As a result, alkaline earth metal-element-free complex oxides with the required functionality have been continually sought after [18].

The state-of-the-art proton-conducting electrolytes are complex BaCeO_3 – BaZrO_3 oxides which exhibit not only a well-known compromise between protonic conductivity (drawback of pure zirconates) and chemical stability (drawback of pure cerates) [19–21], but also the appropriate combination of thermo- and chemical expansion behavior [22,23]. There are representatives of highly stable Ca-, Sr- and Ba-free proton conductors (for example, LaScO_3 [24], LaNbO_4 [25], $\text{La}_2\text{Ce}_2\text{O}_7$ [26]), however they do not compete with BaCeO_3 – BaZrO_3 analogs because of their inferior ionic or undesirable electronic transport.

Among the great variety of electrodes with mixed ionic and

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electronic conductivity, layered $\text{Ln}_2\text{NiO}_{4+\delta}$ nickelates ($\text{Ln} = \text{La}, \text{Pr}$ or Nd) with a K_2NiF_4 -type structure are considered to be one of the most attractive electrodes for PCECs [27–29]. Compared to perovskite-structured cobaltite and ferrite materials, nickelates demonstrate excellent chemical compatibility with both BaCeO_3 - and BaZrO_3 -based electrolytes [30], have low thermal expansion coefficient values [31–33] and high surface exchange and oxygen diffusion coefficients [34,35]. In addition, their tolerance to hydroxide formation (even for systems, doped by alkaline-earth elements) ensures efficient utilization of $\text{Ln}_2\text{NiO}_{4+\delta}$ as oxygen electrodes of PCECs [36].

In this work we report the results of a new combination of oxygen electrode ($\text{Nd}_{1.95}\text{Ba}_{0.05}\text{NiO}_{4+\delta}$) and electrolyte ($\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$) materials for designing the intermediate-temperature PCEC for efficient electricity/hydrogen energy conversion. Along with it, the novelty sign of this work consists in the fact that the fabricated PCEC was characterized not only at weak conditions (one temperature, one operation applied voltage or one set of gas compositions), but under their wide variation, including temperatures (500–750 °C), applied electrolysis potentials (~0.8–2 V) and water vapor partial pressure in anode atmospheres (0.03–0.5 atm). Finally, the PCEC performance was compared in details with those of recently tested PCECs to confirm the attractiveness of the electrochemical cell and materials used.

2. Experimental

2.1. Materials synthesis

$\text{Nd}_{1.95}\text{Ba}_{0.05}\text{NiO}_{4+\delta}$ (NBN) was used as an oxygen electrode material. A slight doping of $\text{Nd}_2\text{NiO}_{4+\delta}$ with the alkaline-earth element was carried out, following a widely used strategy to improve stability and transport properties of the layered nickelates [37,38]. The NBN powder material was synthesized via a citrate-nitrate synthesis method. Nitrates of corresponding metals were completely dissolved in distilled water and then citric acid (CA) was added as a chelating agent, adjusting a mole ratio of 1:2 between total metal cations and CA. The pH value of the resulting solution (~7) was regulated by ammonia. Then the solution was treated at 200 °C, causing water evaporation, gelation and, finally, combustion. The as-prepared ash was thoroughly milled in acetone media (agate mortar, 1 h), calcined at 700 °C to remove and decompose organic residue, then ball-milled (300 rpm, 1 h) and synthesized at 1100 °C for 5 h.

One portion of the powder was used for phase analysis in order to carry out the chemical compatibility study between functional materials and fabricating the electrode layers. Another portion was pressed in bars with dimension parameters of $15 \times 3 \times 3$ mm followed by sintering at 1250 °C for 5 h to study thermal behavior and electrical conductivity.

$\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ (BCZD) powder was obtained according to the similar synthesis route. Its details were thoroughly described in our previous works [29,39]. The BCZD powder was utilized as a source for forming the BCZD electrolyte and Ni-BCZD cathode functional materials of the PCEC. Cermet compositions consisted of powder mixtures of NiO:BCZD (55:45 in weight ratio) and NiO:BCZD:starch (60:40:20 weight ratio) for the preparation of functional and supported substrates of the fuel electrode, respectively.

2.2. Materials characterization

The phase analysis was studied by X-ray diffraction (XRD) analysis using a Rigaku D/MAX-2200VL/PC diffractometer with $\text{Cu K}\alpha$ radiation. The scans were performed between 20 and 80° with a rate of 5°min^{-1} at a step of 0.02°. The XRD analysis was performed for the synthesized powders as well as their calcined mixtures to check chemical compatibility.

Scanning electron microscopy (JSM-5900LV) was used to observe microstructural quality of the functional materials of the PCEC as well

as its integrity.

To evaluate thermal expansion coefficients (TECs), the thermal behavior of the materials was analyzed using a Netzsch DIL 402 PC dilatometer. The data were obtained in cooling mode in a temperature range of 100–1000 °C. Due to high precise of the equipment used, the relative error does not exceed 1% for the dilatometric curves and 5% for TECs.

Total conductivity of NBN was measured by 4-probe DC current method in ambient air atmosphere in a range of 300–900 °C, using a Zirconia-318 microprocessor as a system for resistance (R) measurements. The total conductivity was calculated as

$$\sigma = \frac{L}{a \cdot b} \cdot \frac{1}{R} \quad (1)$$

where a and b are the width and height of the sample and L is the length between the potential probes. The overall error is assumed to be around 5%, which associated with the inaccuracy of determining the dimension parameters of the sample.

2.3. Electrochemical cells fabrication

The symmetrical cell was fabricated using the BCZD electrolyte as support basis with symmetrically formed NBN electrodes. The NBN powder, α -terpineol and ethyl cellulose were thoroughly mixed to prepare the electrode slurry, which was then painted onto both electrolyte surfaces. The electrode sintering was carried out at 1100 °C for 1 h to achieve the appropriate adherence with the electrolyte and maintain the sufficient porosity of the electrode layers.

The PCFC was fabricated by utilizing a tape-calendering method, which is a cost-effective and simple method that makes it attractive for technological scaling. The basic principles for preparing the electrochemical cells based on proton-conducting materials are presented elsewhere [40]. The raw half-cell, consisting of the 500 μm thick supported fuel electrode, 35 μm thick functional fuel electrode and 20 μm thick electrolyte layers was sintered at 1400 °C for 3 h. Then the NBN cathode was formed and sintered in the same way as for fabrication of the symmetrical cell.

2.4. Electrochemical cells characterization

The symmetrical cell was electrochemically tested in dry and wet air atmospheres between 500 and 700 °C. The dry air ($p_{\text{H}_2\text{O}} = 1 \cdot 10^{-4}$ atm) was obtained by passing air through a zeolite column while wet air ($p_{\text{H}_2\text{O}} = 0.03$) was passed through a water bubbler thermostated at 25 °C.

The impedance spectra were recorded by a potentiostat/galvanostat Amel Amel 2550 (Italy) synchronized with a frequency response analyzer (MaterialsM 520, Italy). The frequencies varied between 10^{-2} – 10^6 Hz, the amplitude signal was 50 mV. The impedance spectra obtained were fitted using Zview software with a maximum error of 5% for constitute model parameters (R_j , Q_j , n_j).

The electrochemical cell was tested in an electrolysis mode of operation after complete NiO reduction at 600 °C for 5 h, when a stable steady-state potential was reached. The home-made test system was developed to carry out the electrochemical characterization, which principal scheme is shown in Fig. S1. The i (current density) – U (voltage) data were obtained varying the applied potential from open circuit voltage (OCV) values to 2.000 V with a step of 5 mV and a rate of 2 V min^{-1} . The measurements were performed between 500 and 750 °C with a temperature step of 25 °C using the previously mentioned potentiostat/galvanostat. The composition of fuel (wet hydrogen, $p_{\text{H}_2\text{O}} = 0.03$ atm) was set as a constant, whereas the $p_{\text{H}_2\text{O}}$ level in oxidant was changed up to 0.03, 0.30 or 0.5 atm.

The current interruption technique was successfully used to separate ohmic voltage and electrode overpotential from the total voltage differences, ΔU ($\Delta U = U - U_{\text{OCV}}$, where U is the applied voltage, U_{OCV}

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