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Preparation of Anode Supported Solid Oxide Fuel Cells (SOFCs) Based on BIT07 and Pr₂NiO_{4+δ}: Influence of the Presence of GDC Layer

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Abstract In this work, we study the electrochemical performance of anode supported solid oxide fuel cells (SOFCs) based on perovskite-type materials: BaIn_{0.3}Ti_{0.7}O_{2.85} (BIT07) as an electrolyte, BIT07-Ni as a cermet anode and Pr₂NiO_{4+δ} as a cathode. Anode/electrolyte assemblies have been prepared by tape casting and co-firing and the cathode has been deposited by screen-printing. The performance of BIT07-Ni/BIT07/Pr₂NiO_{4+δ} cells has been determined between 600 and 750 °C under humidified (3% H₂O) hydrogen as fuel and air as oxidant. The presence of an interfacial layer of gadolinia doped ceria (GDC) is also tested. Impedance Spectroscopy (EIS) measurements have also been carried out and allowed to differentiate between the series and polarization resistances. The power density obtained from the cell with GDC was 119.21 mW/cm² at 700 °C, compared with 28.1 mW/cm² for the cell without GDC thin layer. These results confirmed that the presence of a dense thin layer of GDC at the interface electrolyte/cathode is a very promising method for intermediate temperature SOFCs (IT-SOFCs) to increase the performance.

Keywords Tape casting · SOFC · EIS · Pr₂NiO_{4+δ}

Introduction

Nowadays, solid oxide fuel cells (SOFCs) operate at 800–1000 °C. Reducing the operating temperature of solid oxide fuel cells requires the development of new electrolyte materials with good performance at intermediate temperatures (500–700 °C). BaIn_{0.3}Ti_{0.7}O_{2.85} (BIT07) has the required transport properties and redox stability to be considered as a promising electrolyte material with an ionic conductivity of 10⁻² S cm⁻¹ at 700 °C and chemical stability under a wide range of partial pressures of oxygen [1–4]. The praseodymium nickelate Pr₂NiO_{4+δ} (so-called PNO) is a mixed ionic electronic conducting (MIEC) oxide widely studied as oxygen electrode for solid oxide fuel cells and solid oxide electrolysis cells (SOEC) as well. MIEC oxide attracted particular attention since the oxygen reduction reaction (ORR) has been extended to the whole volume of the electrode, compared to a pure electronically conducting cathode where the ORR is restrained to the triple phase boundary (TPB) points located at the cathode/electrolyte interface [5–9].

This paper aims to study the influence of the presence of the material used as an interlayer between the PNO electrode and the BIT07 electrolyte on the electro- chemical performance of the SOFC. $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (namely GDC) has been selected as interlayer material. It has also been demonstrated that BIT07 can be used with well- known cathode materials, such as $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) or $\text{Nd}_2\text{NiO}_{4+\delta}$, and that best results regarding electrochemical performance have been obtained with LSCF.

Our main objective in this work is to prepare a complete Ni-BIT07/BIT07/PNO and Ni-BIT07/BIT07/GDC//PNO cells by tape casting and screen printing. They have been tested under air on the cathode side and wet H_2 (3% H_2O) on the anode side. The performance has been discussed in terms of total resistance determined from current density/voltage curve (J/U) and Electrochemical Impedance Spectroscopy (EIS) measurements at the Open Circuit Voltage (OCV) to understand the origin of this resistance, and to determine the relevant parameters that can be modified in order to minimize it. The stability of the cell presenting the highest performance has been studied at the operating temperature of 700 °C.

Experimental

$\text{BaIn}_{0.3}\text{Ti}_{0.7}\text{O}_{2.85}$ (BIT07) was synthesised by solid state reaction by using stoichiometric amounts of BaCO_3 (Alfa Aesar), In_2O_3 (Alfa Aesar) and TiO_2 (Merck). Reactants were thoroughly mixed using acetone in an agate mortar and calcined at 1200 °C for 24 h. The obtained powder was again ground well, mixed, pressed into disks and sintered at 1350 °C for 24 h, ground and passed through mesh 100. $\text{Pr}_2\text{NiO}_{4+\delta}$ powder was provided by Marion Technologie and NiO powder (grain size 0.5–1 μm) was provided by Pharmacie Centrale de France. X-ray diffraction (XRD) was used to characterize the structure of the as-prepared powders. The patterns were obtained using a Brüker “D8 Advance” powder diffractometer with a Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) and 2θ varying from 20 to 80° by steps increments of 0.0146° and 0.2 s counting time per step. The Scanning Electron Microscopy (SEM) was performed on a FEG-SEM JEOL 7600. By Brunauer–Emmett–Teller (BET), the surface areas of the powders were measured and carried out on a Micromeritics 3Flex analyzer determined by N_2 adsorption–desorption isotherm measurement at –196°C.

Before cell fabrication and in order to decrease the grain sizes, the as-prepared powders of BIT07 were ball-milled at 500 rpm: 60 h. The anode composition has been

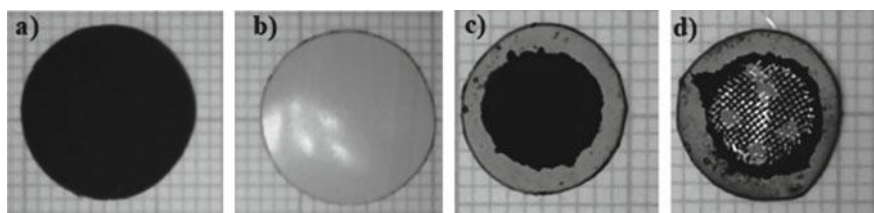


Fig. 3.1 Preparation of Ni-BIT07/BIT07/PNO anode supported cell. **a** Anode of BIT07-NiO, **b** electrolyte BIT07, **c** deposition of PNO cathode, **d** current collector of gold grid

optimized to reach the best electrochemical performance, obtained with a BIT07- Ni cermet (BIT07:NiO 50:50 wt%), realized with a BIT07 powder ball-milled and 5 wt% CB as pore forming agent. The button cell (\varnothing 10 mm) is composed of an anode

supported electrolyte/anode half-cell, prepared by tape casting and co-fired. Then a PNO cathode is deposited on the electrolyte by screen-printing (Fig. 3.1).

Current collectors, made of discs (5 mm in diameter) of gold grid (Goodfellow, wire diameter: 60 μm) are attached on both the electrodes using gold ink. The cell is placed at 120 $^{\circ}\text{C}$ for overnight to evaporate the solvents and to obtain good electrical contacts. The current–voltage characteristic is measured with the use of a laboratory- made testing system. The cell was sealed on the top of an alumina sample tube. Thus separating the atmospheres between the inside and outside of the tube. The fuel-gas supply tube is situated inside the sample tube. The system was kept vertically in a tubular furnace. The measurements of current density (J) and voltage (U) were done by digital multimeters Keithley 197 and Protek 506, respectively. Current drawn in the circuit was varied using a rheostat. Prior to the measurements, nickel oxide is reduced in situ at 700 $^{\circ}\text{C}$ for 2 h under wet H_2 and measurements were made at 700 $^{\circ}\text{C}$, under wet (3% H_2O) H_2 on the anode side, and air on the cathode side.

Electrochemical performances of single cells were studied by electrochemical impedance spectroscopy (EIS). The measurements were realized using a frequency response analyzer Solartron 1260. The impedance spectra were recorded over a frequency range 2 MHz to 0.01 Hz with a signal amplitude of 10 mV and with 10 points per decade under open circuit conditions from 500 to 700 $^{\circ}\text{C}$. The EIS diagrams were normalized to the electrode area and fitted using equivalent circuits with the ZView[®] software (Scribner Associates). Post mortem (after measurements) analyses of the cells have been carried out by SEM, using a JEOL 7600.

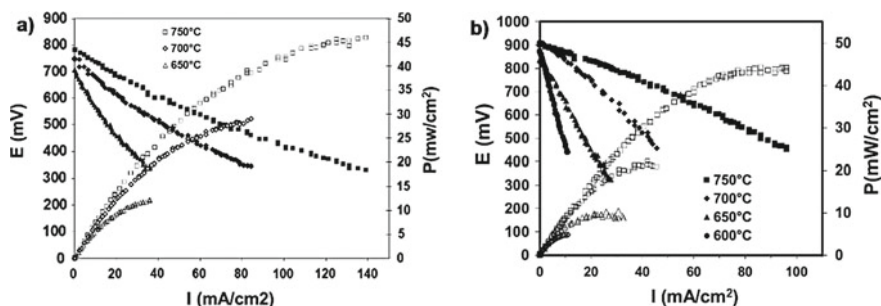


Fig. 3.2 Performance of a single cell consisting in: **a** Ni-BIT07/BIT07 and $\text{Pr}_2\text{NiO}_{4+\delta}$ sintered at 1050 $^{\circ}\text{C}$, **b** Ni-BIT07/BIT07 and $\text{Pr}_2\text{NiO}_{4+\delta}$ sintered at 1100 $^{\circ}\text{C}$ as the cathode; I-V curves and resulting power densities

Results and Discussion

Characterization of Material

Figure 3.2 presents the voltage (U) and power density (P) versus current density (J) characteristics obtained for two single cells at different temperatures 1050 and 1100 $^{\circ}\text{C}$, respectively, Fig. 3.2a, b. In both cases, the polarisation curves (U/J) are clearly linear in the studied current density range. In both cases, the OCV is lower than the theoretical value expected, suggesting a small leakage between gas chambers. Table 3.1 gathers the cells characteristics obtained from the voltage and power density versus current

density characteristics and also from the Nyquist diagrams of the single cells.

The extrapolated maximum power densities are of about 28.1 and 22.06 mW cm⁻² for the two cells, respectively. The ASR value obtained from the EIS measurements, 10.41 for cells A at 700 °C, is in agreement with the ones obtained from the U/J

Table 3.1 Characteristics of the cell Ni-BIT07/BIT07 and Pr₂NiO_{4+δ} sintered at 1050 °C recorded at OCV, ASR(U/J) calculated from U/J curves, ASR(EIS), Rs and Rp obtained from the EIS measurements

T (°C)	OCV (V)	P _{max} (mW cm ⁻²)	ASR _(U-J) (Q cm ²)	ASR _(Nyquist) (Q cm ²)	Re.S (Q cm ²)	Rp.S (Q cm ²)
600	0.875	4.83	41.34	43.39	3.46 (7.4%)	39.93 (92.6%)
650	0.843	9.85	18.81	20.27	2.20 (9.8%)	18.07 (90.2%)
700	0.914	22.06	9.75	10.41	1.01 (8.8%)	9.40 (91.2%)
750	0.900	44.13	4.64	5.63	1.14 (16.8%)	4.49 (83.2%)

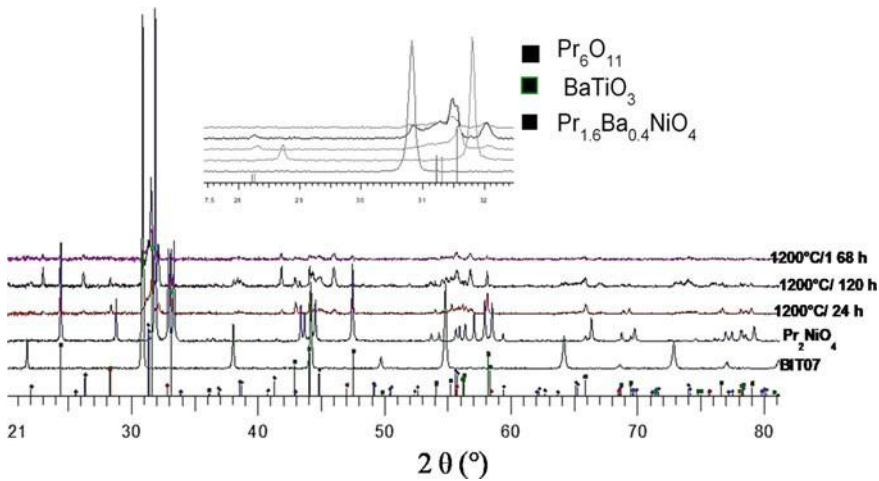


Fig. 3.3 X-ray diffraction patterns of BIT07/Pr₂NiO_{4+δ} composite pellets that were calcined at 1100 °C for different times

curves, 9.95. Those values are too high with a major contribution of polarization resistance (91.2%) and need more improvement. Thus indicates that the polarization resistance played an important role in cell performance.

In order to understand the origin of the low performances of the two cells, the reactivity test between BIT07 and Pr₂NiO_{4+δ} powders for more than 168 h at 1100 °C was done as shown in Fig. 3.3. Indeed, the DRX analysis reveals the significant presence of a new phase (Pr_{1.6}Ba_{0.4}NiO₄) due to the reaction between the electrolyte and cathode. Considering the reactivity of the Pr₂NiO_{4+δ} with BIT07, the higher power densities would expect to be achieved by using a thin interfacial layer of GDC.

A thin interfacial layer (5 μm) of GDC is deposited to the electrolyte/anode half-

cell by screen-printing and co-fired at 1350 °C for 8 h. Then a PNO cathode is deposited on the electrolyte by screen-printing. To demonstrate the benefit of incorporating a thin layer at the interface between the electrode and electrolyte, the I–V–P curves of the fuel cell are shown in Fig. 3.4. The power density obtained from the cell with GDC thin film was about 119.21 mW/cm² at 700 °C, compared with about 28.1 mW/cm² for the cell without thin film.

Conclusion

In this work, anode supported cells based on BIT07 as an electrolyte, BIT07-Ni as anode and Pr₂NiO_{4+δ} as cathode have been successfully realized by tape casting and screen-printing. The reactivity test between BIT07 and Pr₂NiO_{4+δ} powders reveals the presence of a new phase (Pr_{1.6}Ba_{0.4}NiO₄) which explain the low performances of the single cell. The power density of a single cell with GDC thin film at the interface electrolyte/cathode

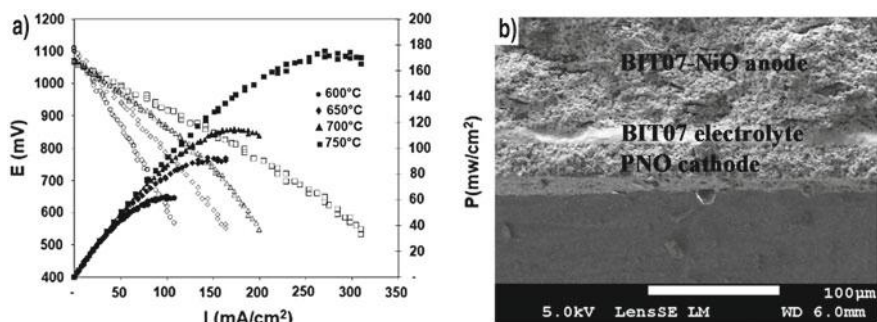


Fig. 3.4 a Performance of a single cell consisting in Ni-BIT07/BIT07/GDC/Pr₂NiO_{4+δ}; I-V curves and resulting power densities, b scanning electron microscope image (cross-section) of single cell

was significantly higher than that of a single cell without interfacial layer. This is attributed to increased interfacial area. The factors such as the better electrocatalytic activity of ceria and the intrinsic properties of nanostructured thin films.

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