

Anodic Layers Based on Doped-Ceria/Ni Cermet for Direct Ethanol Fuel Cells

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Ceria-based/Ni cermets were studied as the catalytic layer deposited onto the standard yttria-stabilized zirconia/Ni anode for direct ethanol solid oxide fuel cells. The influence of the dopant on both Zr- and Nb-doped (10 mol%) ceria and pure ceria was investigated on the properties of cermets with Ni ~15% volume fraction. Electrolyte-supported fuel cells with ceria-based/Ni catalytic layer were tested for ~100 hours under (dry) ethanol. Fuel cells using the different ceria/Ni cermets showed excellent stability on ethanol, irrespectively of the different properties of the ceramic phase of the catalytic layer. Fuel cells results confirmed that the studied ceria-based cermets are stable catalysts towards ethanol steam reforming.

Introduction

Ethanol is a promising fuel for solid oxide fuel cells (SOFCs) (1-3). Ethanol brings together important advantages of both liquid and renewable fuel that can be obtained from different biomasses. It is widely produced and distributed in countries like USA and Brazil with a marked use in transportation. Particularly, ethanol derived from sugar-cane is both economically and energetically viable biofuel that can bring important economic and environmental advantages. Recently, it was announced new prototype car based on ethanol SOFC (4). This new carbon-neutral concept vehicle uses bioethanol and a low-power SOFC to generate electricity onboard that extends considerably the range of a battery-powered electric motor.

The main challenge of using ethanol in SOFCs is to avoid coking on the anode. Standard anodes based on Ni cermets form carbon deposits that result in the failure of the device (5,6). However, Ni-based cermets exhibit the best electrochemical performance on hydrogen and are industrially developed components for SOFCs. Thus, keeping the standard cermet in the anode is a desirable feature, especially considering that alternative coke-resistant anodes still require improvements for high-performance (5).

Latest generation of SOFCs is a multilayer device in which several functional layers were incorporated to the standard anode/electrolyte/cathode configuration. In addition to the electrode functional layers, diffusion barriers and protective coatings have become important components for high-performance SOFC. Therefore, using a catalytic active layer that enables the fuel cell to run using a renewable fuel such as bioethanol is a reasonable strategy (7,8). Thus, separating the catalytic and electrochemical reactions in different anodic layers has two main advantages: keeping the high-performance YSZ/Ni cermet and allowing an optimized catalyst for ethanol reforming (7). Doped-cerium oxide is an attractive ceramic material for solid oxide fuel cells (SOFCs) because of the excellent electrochemical and catalytic properties, and good compatibility with remaining cell components. In the present study, we have investigated the effect of different dopants on the properties of ceria-based Ni cermets aiming at using such composites as the catalyst for ethanol internal reforming in SOFCs. Cermets with 18 wt.% Ni supported on ceria and ceria doped with Zr and Nb (10 mol%) were studied. Such relatively low Ni volume fraction (~15 vol.%) aims at minimizing coke formation while promoting electronic conductivity. Post-test analyses evidenced that water electrochemically generated promotes ethanol reforming, in agreement with catalytic tests in which doped-ceria/Ni showed no evidence of carbon deposits in the steam reforming reaction.

Experimental

Ceria and ceria doped with 10 mol% Nb or Zr were synthesized by a hydrothermal method (8,9). Cerium and the dopant hydroxides were co-precipitated by the addition of an excess of ammonium hydroxide. The precipitate was treated in an autoclave at 453 K for 4 h. Then, the precipitate was washed with distilled water and calcined at 573 K for 2 h. Ni was added to doped-ceria by wet impregnation using an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to obtain 18 wt.% of Ni. The composite sample was dried at 393 K and calcined under air (50 mL/min) at 1473 K for 5 hours. X-rays diffraction (XRD) data were collected in a Rigaku Miniflex diffractometer, using $\text{CuK}\alpha$ radiation in the 2θ range between 25° - 80° with step size 0.04°s^{-1} and 1 s/step counting time for both calcined and reduced samples (H_2 flow at 1023 K for 1 h). Temperature programmed reduction (TPR) measurements were carried out in a homemade apparatus. The catalyst was pre-treated at 673 K for 1 h under air flow prior to the TPR experiment in order to remove traces of water. The reducing mixture (2% H_2/N_2) was flown through the sample (80 mg) at a flow rate of 30 mL min^{-1} and the temperature was increased to 1273 K with a heating rate of 10 K min^{-1} .

Electrolyte-supported single cells were fabricated using 8 mol% yttria-stabilized zirconia (YSZ, Tosoh, Japan) cylindrical substrates, sintered at 1873 K, with final dimensions 18 mm diameter and ~0.5 mm thickness. Using electrolyte-supported fuel cells was preferred to evaluate the stability towards ethanol rather than having high-performance. Electrode layers were deposited by spin-coating using suspensions based on terpeneol and ethyl cellulose (9). The anode functional layer YSZ/NiO (60/40 wt.%) and current collector layer (40/60 wt.%) were deposited and sintered at 1723 K and 1673 K, respectively, for 2 h. $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) cathodes were deposited over a functional YSZ/LSM (50/50 wt.%) composite layer deposited onto the electrolyte and sintered at 1423 K in air for 1 hour. Single cells had a catalytic layer in which the Ni/doped-ceria layer was the active component for fuel processing deposited as an additional outer layer

over the YSZ/Ni anode (7,10-13). Such a catalytic layer avoids direct contact of the fuel with the Ni/YSZ anode and promotes the ethanol reforming (10-13). Anode current collection with Au ink and wires was made in the anode current collector layer before deposition of the catalytic layer. Thus, the catalytic layer has no influence on the electrical properties of the single cell. The Ni/doped-ceria catalytic layer was deposited by spin coating and fired at 1073 K in argon flow for 1 hour (9). Pt mesh current collectors were attached using Pt ink to the surface of cathode, followed by curing at 1073 K. The single cell, with active electrode area of 0.78 cm^2 , was sealed on the tip of an alumina tube sample holder using Aremco 552 cement, with the anode side facing the inner part of the tube. The alumina tube with the sealed single cell was inserted into a resistive horizontal tube furnace and connected to the metallic heads of a homemade test station. During all fuel cell tests, synthetic air was delivered to the cathode with 50 mL min^{-1} flow rate. The single cell was heated up to 1123 K under N_2 flow and then changed to H_2 (3 vol.% H_2O), with 50 mL min^{-1} flow rate, for anode reduction and system stabilization. Temperature was monitored by a thermocouple (type K) placed close to the cathode side and gas flow rates were set by mass flow controllers. Polarization curves were taken during the initial operation on hydrogen using a Zahner IM6 potentiostat. At 1123 K, the fuel cell was polarized at 0.6 V and hydrogen was switched to dry ethanol carried by flowing N_2 . Ethanol was gasified by bubbling N_2 (42 mL min^{-1}) through a saturator containing anhydrous ethanol at 313 K to obtain a gas composition of ~17% of ethanol in nitrogen, with total flow (N_2 +ethanol) of $\sim 50 \text{ mL min}^{-1}$. This ethanol concentration is set to keep the theoretical number of electrons constant for both fuels: hydrogen (100%) and ethanol (17%) (12). The single cells were continuously operated for different time on stream (TOS) while the current density (i) at 0.6 V was monitored for evaluating the stability in direct (dry) ethanol. SEM analyses of the fractured surfaces of the anode were carried out after fuel cell operation to examine possible carbon deposits.

Results and Discussion

The X-rays diffractograms of the calcined samples are shown in Fig. 1. The diffraction lines of CeO_2 with cubic structure (ICSD 34-394) and NiO phase (JCPDS 24018) were observed for NiO/ CeO_2 , NiO/CeNb and NiO/CeZr samples. In addition, the characteristic peaks of ceria are shifted to higher 2θ position for Ni/CeZr, indicating the formation of a solid solution. This was not observed for Ni/CeNb sample, in which it was detected the peaks corresponding to monoclinic phase of CeNbO_4 (PDF 01-072-0905) and nickel niobate phase (ICSD 37-213). These results are an indication that the solubility limit of Nb in ceria was exceeded and Nb reacted with Ni and Ce forming secondary phases. Upon reduction NiO is converted in Ni and only the CeNbO_4 remains as a second phase in the Ni/CeNb sample.

Calculated values of crystallite size are listed in Table 1. Crystallite sizes of ceria increases upon reduction whereas for Ni and NiO no significant changes were observed upon reduction. Nonetheless, it is worth noting that the smallest Ni crystallite size was obtained for Nb-doped sample.

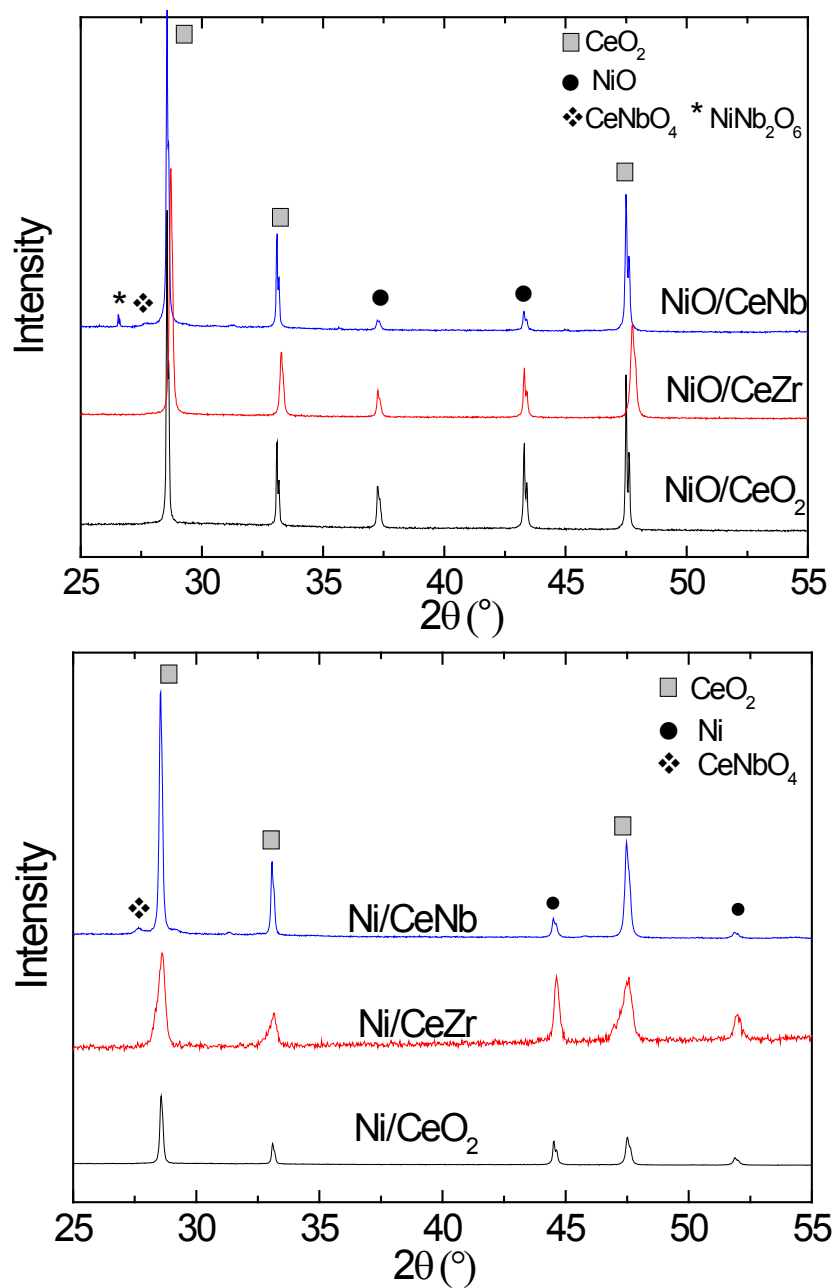


Figure 1. X-rays diffraction patterns of Ni/doped-ceria cermet before and after reduction.

TABLE I. Ceria lattice parameter and crystallite sizes calculated from XRD data.

Sample	$d_{\text{NiO}} / d_{\text{Ni}}$ (nm)	d_{CeO_2} (nm)
NiO/CeO ₂	156	225
NiO/CeZr	113	80
NiO/CeNb	84	130
Ni/CeO ₂	106	166
Ni/CeZr	118	162
Ni/CeNb	89	227

The TPR profiles of calcined composites are shown in Figure 2. The TPR profile of NiO was measured as a reference. The TPR profile of NiO exhibited a more pronounced reduction peak at ~ 650 K and a shoulder at 700 K. The TPR profiles of the ceria supports (not shown) exhibited hydrogen consumption peaks at much higher temperature (>1000 K) for ceria and Zr-doped ceria, whereas Nb-doped ceria exhibited a small H_2 consumption between 600 and 900 K and a broad peak at ~ 1150 K (13).

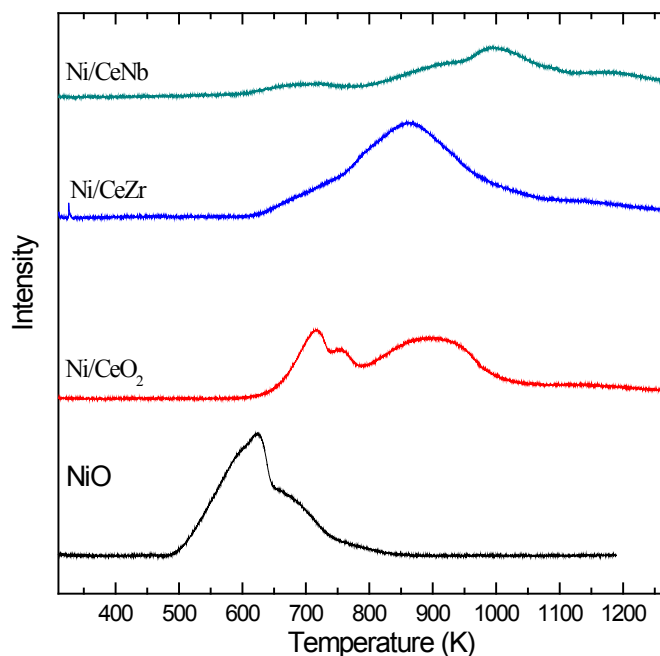


Figure 2. TPR profiles of Ni/doped-ceria cermets.

The TPR of both Ni/CeO₂ and Ni/CeZr (Figure 2) show two main reduction peaks in the 650 - 1000 K temperature range mainly related to the NiO reduction to Ni. The experimental data indicates that NiO was completely reduced. However, Ni/CeNb showed only small peaks of H_2 consumption occurring at higher temperatures and a lower reduction degree. Such a feature is related to the formation of NiNb₂O₆, which reduces at higher temperatures (>773 K) (13).

The electrical properties of the doped-ceria ceramics were investigated by impedance spectroscopy measurements. Fig. 3 shows the Arrhenius plots of ceria-based ceramic supports measured in N_2 flow. The electrical conductivity of the ceria-based samples exhibited characteristic features in agreement with previous reported data (14,15). All samples have thermally activated behavior of the electrical conductivity that was fitted to an Arrhenius-type transport. The ceria-based oxides are known to exhibit high oxygen ion conductivity that is improved by doping with cations, such as Gd, Y, Zr, etc (15). Differently, Nb-doped ceria was previously reported to exhibit a large electronic component of the electrical conductivity (14). In the present study, it was confirmed the expected increase of the conductivity of ceria by Zr doping, which increases the oxygen storage capacity (16). The calculated activation energy E_a values reflect such features. Both ceria and Zr-doped ceria samples have typical values for O^{2-} conductors ($E_a \sim 1$ eV). Differently, Nb-doped ceria has a much lower $E_a \sim 0.3$ eV associated with a higher electrical conductivity, characteristics of mixed ionic-electronic conductor (14,17). Thus,

the ceria dopant has a pronounced effect on the electrical properties of the support, changing both the magnitude and the available charge carriers. The addition of NiO to the doped-ceria increased the electrical conductivity due to the semiconducting properties of NiO. However, the electrical conductivity of NiO/doped-ceria (not shown) is strongly dependent on the electrical conductivity of the ceramic phase because Ni (15 vol.%) has not attained the percolation threshold in the cermets.

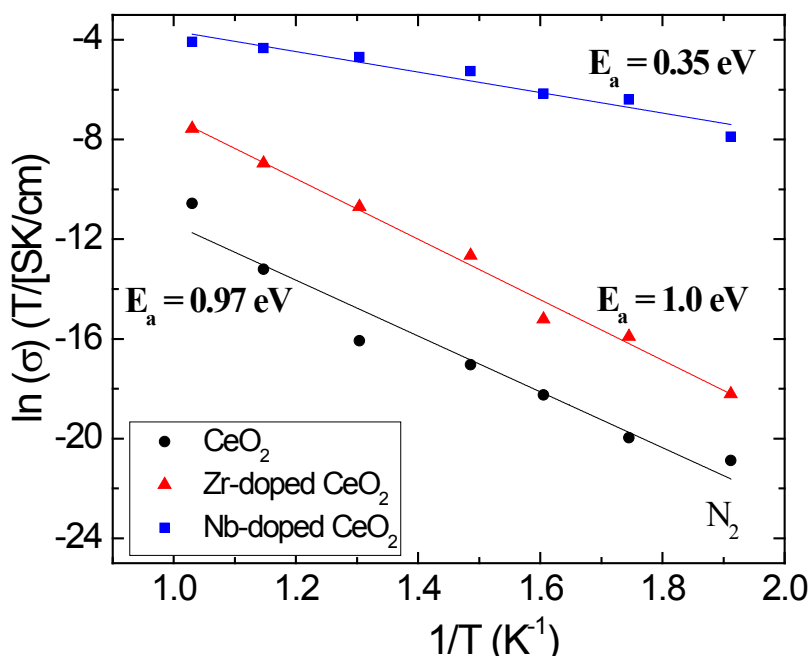


Figure 3. Arrhenius plot of the electrical conductivity of doped-ceria in N₂.

The Ni/doped-ceria catalysts were tested in direct ethanol SOFC. Single cells were initially run on H₂ for anode reduction and system stabilization. After stabilization at 1123 K all samples attained OCV ~1.1 V, close to the theoretical value for H₂ (3 vol.% H₂O). Fuel cells were polarized at 0.6 V and after ~15 hours H₂ was switched to ethanol (dry). The current density *i* at 0.6 V was monitored and fuel cell was continuously operated for long-term stability tests on ethanol (~100 hours). Figs. 4a-4c show *i* as a function of the operating time at 1123 K for the different catalysts. As a general trend, fuel cells were observed to increase the current output during the initial ~10 hours operation under H₂. Such an increase is in agreement with a possible slow kinetics of the reduction of the anodic layers, a feature possibly associated with a relatively low porosity of the anode layers attained during the fuel cell fabrication. The low porosity of the NiO/doped-ceria layer hinders the reduction of the anode inner layers during the initial hours of operation under hydrogen. Probably, as the Ni reduction develops, anode porosity increases and enhances the triple phase boundaries in the anode/electrolyte interface, resulting in higher current output. This is in agreement with dilatometry results (not shown) that revealed a high sinterability of the Ni/doped-ceria compacts, with onset of linear retraction occurring at T~773 K, well below the temperature used for fuel cell fabrication (18).

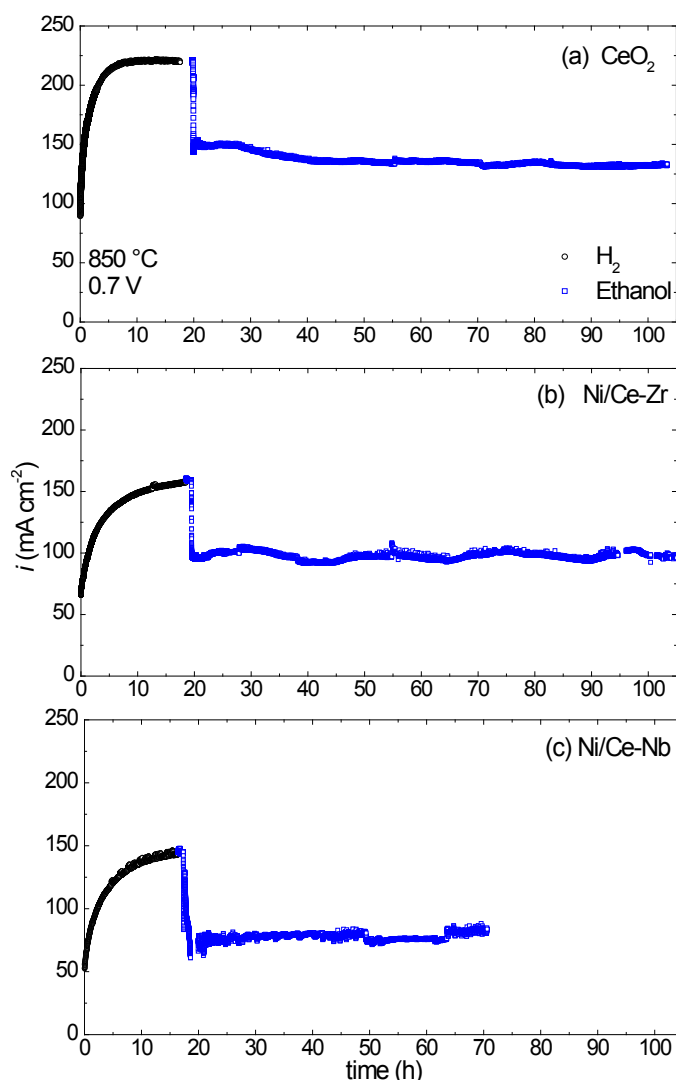


Figure 4. Potentiostatic curves of direct ethanol SOFC using Ni/doped-ceria catalytic layers.

When hydrogen was changed to dry ethanol, a decrease of the current density was observed as a sharp drop of i ($\sim 30\%$). It is important to consider that ethanol is delivered to the fuel cell at 1/6 ratio with respect to H₂ in order to keep the theoretical number of electrons constant (12). In previous studies using porous catalytic layers (25 μm thick) the current output in both H₂ and ethanol was similar (11,12). This was an evidence that ethanol was steam-reformed in the catalytic layer and the produced hydrogen was electrochemically oxidized with good Faradaic efficiency (utilization factor $U_f \sim 37\%$) (11,12). In this present study, changing H₂ to ethanol decreased the current output of the fuel cell, a feature that requires further investigation. Two possible reasons could be pointed out for such a decrease of i on ethanol: i) an U_f that provides less water than the stoichiometry for steam reforming (3:1 water/ethanol) or ii) a decreased OCV caused by direct contact of ethanol (or its decomposition products) with the YSZ/Ni due to an insufficient thickness of the catalytic layer.

The thickness of the catalytic layers was kept to a few microns ($\sim 5\text{-}10 \mu\text{m}$) in order to evidence any possible degradation due to carbon deposits. The Ni/ceria-based powders were observed to have different crystallite size and specific surface area (19). Such

characteristics made a hard task to produce catalytic layers with the same microstructural properties to allow a more direct comparison between the different samples. Nevertheless, as compared to the other samples, the lower current output of the sample using Nb-doped catalytic layer is probably related to the formation of secondary phases, as discussed in Fig. 1.

The most important result in Fig. 4 is the stability of fuel cells running on dry ethanol. All studied fuel cells performed with excellent stability during the test on ethanol, without the addition of water or any other oxidant agent. Fuel cells were operated for ~80 hours on dry ethanol, with the exception of one experiment interrupted at ~70 hours due to power failure. It is important to consider that carbon deposits have been previously reported to form during the initial hours of testing under carbon containing fuels such as hydrocarbons and ethanol (6). In this present study, the stability of the Ni/doped-ceria cermets in fuel cell conditions was measured for times greatly exceeding the typical interval for observing fuel cell collapse due to carbon deposit formation.

The stability of fuel cells is a strong indication that the Ni/doped-ceria cermets were efficient catalysts to avoid carbon deposit formation in the operating conditions of the fuel cells. This is expected since the electrochemical oxidation of hydrogen produces water in excess for the stoichiometry of ethanol steam reforming reaction (12). Thus, under polarization at 0.6 V the fuel cell can resemble the conditions observed in the steam reforming reactions (10,12). In such conditions Ni/doped-ceria cermets were previously reported to be stable with no significant formation of carbon (10). On the other hand, recent results showed that Ni/doped-ceria catalysts deactivate when no water is present for reforming reaction (10,19). Similarly to the catalytic tests in steam reforming conditions, no carbon deposits were identified during fuel cell durability tests on dry ethanol because water was provided by the electrochemical oxidation of hydrogen at the anode/electrolyte interface (10, 19). According to catalytic tests (not shown), cermets promoted complete conversion of ethanol with comparable distribution of products (mainly H₂, CO, CO₂, and water) and similar selectivity to hydrogen (~60%). The main difference concerning the investigated ceria dopants was related to the electrical properties, as shown in Fig. 3. Such different transport properties are related to the defects (ionic and electronic) induced by the dopants in the ceria lattice that strongly affect both the transport and catalytic properties. Thus, the experimental data suggest that although the ceria supports exhibit very different properties, the determining factors for fuel cell electrochemical performance is the catalytic properties of the metallic phase. The fuel cell tests showed that the water resulting from the electrochemical reaction at the anode/electrolyte sustain the catalytic internal steam reforming in SOFCs.

Conclusions

Nickel/doped-ceria cermets were used as catalytic active layers for direct ethanol SOFCs. By using different dopants results in distinct chemistry of defects (ionic and/or electronic) in ceria that affects both the charge carriers for electrical transport and the available species for catalytic reactions. In spite of such differences, the direct ethanol SOFCs were very stable running on dry ethanol, showing no evidence of carbon deposition. Such results confirms that Ni/doped-ceria cermet is stable catalyst provided water is provided for ethanol steam internal reforming.

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