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Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 1: Fuel Cell Basics / Fuel Infrastructures
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-1
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-651-4

Development of Fe-Ni/YSZ-GDC Electro-catalysts for Application as SOFC Anodes: XRD and TPR Characterization, and Evaluation in Ethanol Steam Reforming Reaction

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Abstract

Electro-catalysts based on Fe–Ni alloys were prepared using physical mixture and modified Pechini methods; they were supported on a composite of Yttria Stabilized Zirconia (YSZ) and Gadolinia Doped Ceria (GDC). The composites had compositions of 35% metal load and 65% support (70% wt. YSZ and 30% wt. GDC mixture) (cermets). The samples were characterized by Temperature-Programmed Reduction (TPR) and X-Ray Diffraction (XRD) and evaluated in ethanol steam reforming at 650 °C for six hours and in the temperature range 300 – 900 °C. The XRD results showed that the bimetallic sample calcined at 800 °C formed a mixed oxide ($NiFe_2O_4$) in spinel structure; after reducing the sample in hydrogen, Ni-Fe alloys were formed. The presence of Ni decreased the final reduction temperature of the $NiFe_2O_4$ species. The addition of Fe to Ni anchored to YSZ-GDC increased the hydrogen production and inhibits the carbon deposition. The bimetallic 30Fe5Ni samples reached an ethanol conversion of about 95%, and a hydrogen yield up to 48% at 750 °C. In general, the ethanol conversion and hydrogen production were independent of the metal content in the electro-catalyst. However, the substitution of Ni for Fe significantly reduced the carbon deposition on the electro-catalyst: 74, 31, and 9 wt. % in the 35Ni, 20Fe15Ni, and 30Fe5Ni samples, respectively.

Keywords

Anode; Carbon deposition; Ethanol; Solid oxide fuel cell (SOFC); Fe–Ni catalyst; Ethanol Reforming; X-ray diffraction

1 Introduction

Solid oxide fuel cells (SOFC) are devices that convert the chemical energy of gaseous fuels, such as hydrogen, natural gas, and ethanol, to electricity through electrochemical processes. Due to their high efficiency, design modularity, and environmentally friendly nature, SOFCs are considered one of the most promising energy converters. In addition, the SOFC compared to other fuel cell systems offers the possibility of internal reforming of ethanol or

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hydrocarbon fuels, which may occur directly on the anode; this provides SOFC with great flexibility in terms of fuel choice, one of its main advantages [1-5].

One of the challenges of using fuel cells as a commercial alternative for electricity generation is the fact that they usually require hydrogen as fuel. Hydrogen is predominantly produced by steam reforming reaction of natural gas or higher hydrocarbons, with carbon monoxide contents of around 100 ppm. Therefore, hydrogen production and distribution add additional levels of complexity to the overall system. However, oxidation of ethanol and hydrocarbons directly on SOFC anodes has been experimentally demonstrated by a number of authors [6-10]. It is well known that Ni–YSZ cermet anodes of SOFC have excellent catalytic properties and stability for H_2 oxidation in SOFC operation conditions [11, 12]. However, as Ni is also a good catalyst for hydrocarbon cracking reaction, the use of ethanol or hydrocarbon fuels in a SOFC with a Ni-based anode results in very fast carbon deposition, with irreversible cell degradation [13-16]. Therefore, the development of an anode material for SOFCs that operates on ethanol or hydrocarbons at lower carbon to water ratios is widely recognized to be an important technical objective [3, 7, 8, 17, 18].

2 Experimental

2.1 Sample preparation

Ni-Fe/YSZ-GDC cermets, with 35 wt. % of metal supported on YSZ-GDC (70 wt. % of YSZ), were prepared using two different methods. YSZ [$(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$], surface area 6 - 9 m^2/g and particle size 0.5 - 0.7 µm, and GDC ($Ce_{0.9}Gd_{0.1}O_2$), surface area 5 - 8 m^2/g and particle size 0.3 - 0.5 µm powders, were obtained from Fuel Cell Material®.

Modified Pechini method for sample preparation started with an aqueous solution of Ni and Fe nitrate to which was added a solution of citric acid (CA). The resulting solution was stirred and heated to 60 °C when the support (YSZ-GDC) was added. Ethylene glycol (EG) was added to the solution in a molar ratio of CA/EG = 1/4, with a molar ratio of CA/metallic ion = 6/1, followed by stirring at 60 °C for one hour; the temperature was raised to 90 °C and kept at this temperature until the final volume was reduced to half its initial value. The polymeric gel formed was calcined at 350 °C, at a heating rate of 1 °C/min. Afterwards, the obtained brown solid was ground in a ball mill for 24 hours and calcined at 900 °C for three hours, with a heating rate of 5 °C/min.

Physical method for sample preparation used YSZ-GDC mixed with NiO in the presence of a small amount of ethanol; the mixture was stirred for 24 hours in a ball mill. The powder formed was calcined at 900 °C for 3 hours, with a heating rate of 5 °C/min.

2.2 Sample characterization

Sample crystallographic characterization was performed by XRD in a Shimadzu XRD 6000 equipped with Cu-Ka radiation (40 kV and 40 mA) between 10 and 80° at a rate of 0.25 °C/min[1].

TPR analysis was performed on a system consisting of a quartz reactor in a "U" shape, an oven with temperature control and a gas analysis system with thermal conductivity detector (TCD). The sample was placed in the quartz reactor, and heated from ambient temperature to about 1000 °C at a heating rate of 10 °C/min under a flow of 1.5% H_2/argon at a rate of

30 ml/min. The spectra were treated with deconvolution techniques to determine the different species present in the solids.

The measurements of specific surface area were performed in a Micromeritics ASAP 2020, using samples preheated to 300 °C for one hour under nitrogen flow.

2.3 Catalytic tests

The samples were evaluated in ethanol steam reforming in function of time on stream at 650 °C for six hours in a quartz micro-reactor. Initially the catalyst was reduced *in situ* with H_2 (10 mol%) diluted in N_2, between 30 and 800 °C with a heating rate of 10 °C/min and maintained at this temperature for 30 minutes. N_2 at a flow of 60 mL/min was the carrier gas. An ethanol aqueous solution, with a 3:1 molar ratio of water to ethanol, was injected into the reaction system through a syringe-type pump; the ethanol injection rate was 1.78×10^{-2} mol/hour. The gaseous products were analyzed by gas chromatography (SHIMADZU GC-17A), with an automatic sample injection.

3 Results and Discussion

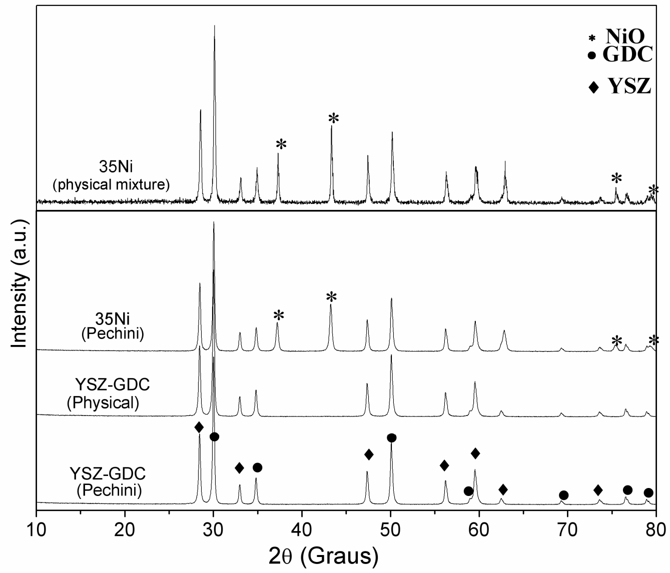


Figure 1: **XRD patterns of Ni/YSZ-GDC, prepared by the physical mixture and Pechini methods and YSZ-GDC after calcination.**

Figure 1 shows the XRD spectra of 35Ni, 35NiC and YSZ-GDC support. In both samples, NiO in the cubic form (JCPDS 78-0643) was formed following the calcination step; YSZ (JCPDS 82-1246) and GDC (JCPDS 75-0161) were both in the cubic form. Figure 2 shows the XRD patterns for the samples containing Fe. Only hematite in the rhombohedral structure (JCPDS 87-1166) was present in 35Fe sample. The XRD patterns of bimetallic samples indicated the coexistence of hematite and a mixed oxide of Ni and Fe ($NiFe_2O_4$), with a spinel-type cubic structure (JCPDS 74-2081). Figure 3 shows the XRD patterns of the samples after reduction in presence of H_2 at 800 °C. Ni in 35Ni sample was crystallized with

FCC structure (JCPDS 87-0712); Fe in 35Fe sample was crystallized with BCC structure (JCPDS 87-0722).

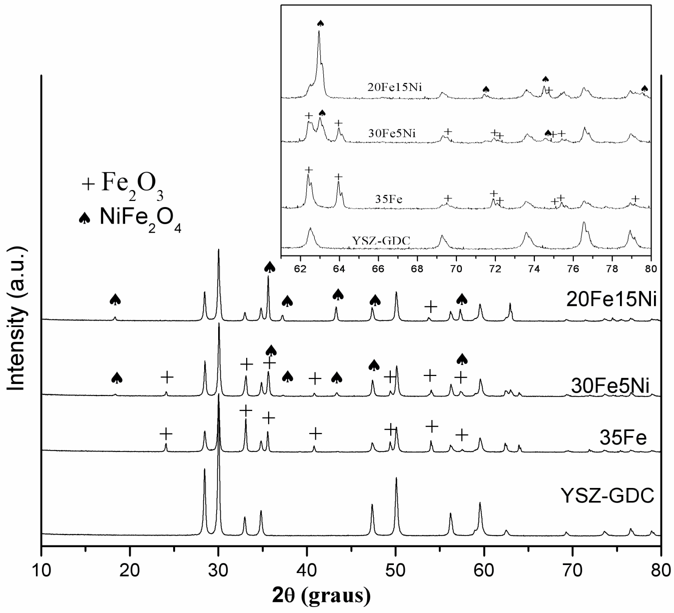


Figure 2: XRD patterns of Fe/YSZ-GDC prepared by Pechini method after calcination.

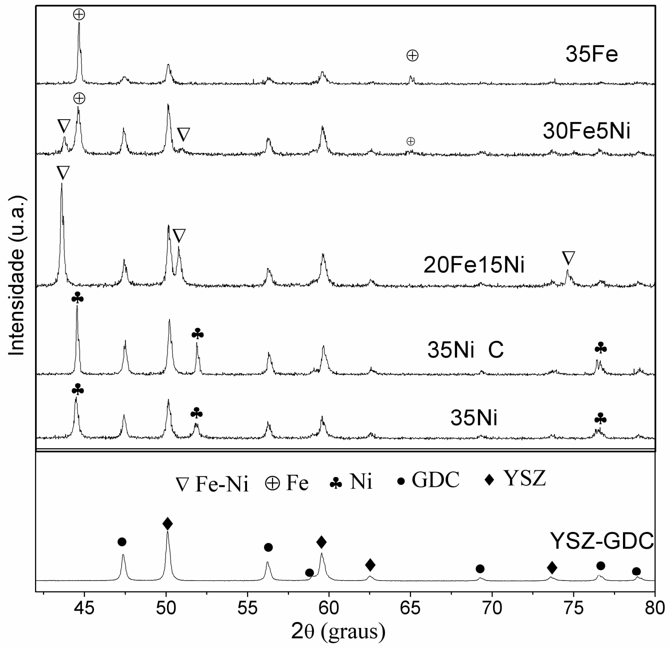


Figure 3: XRD patterns of electro-catalysts after reduction [24].

The XRD diffractogram for 20Fe15Ni (Figure 3) presented three new peaks at 2θ = 43.60, 50.84 and 74.69°, suggesting the formation of a Ni-Fe alloy (CAPES 26009) [24]; this alloy exhibited an FCC crystal structure. Similarly for 30Fe5Ni, peaks in the same positions were observed, indicating the formation of a Ni-Fe alloy with FCC structure and suggesting that Fe replaced Ni in the unit cell. Additionally, the peaks remained in 2θ = 44.72 and 65.13°, characteristic of BCC Fe, might imply that there was phase segregation for the metallic phase of 30Fe5Ni: Ni-Fe alloy and pure Fe.

Figure 4 shows the TPR profiles for the studied materials. As the TPR curve for the support (YSZ-GDC) showed no event associated with reduction, the peaks that appeared in the sample TPR curve were attributed to the reduction of Ni and Fe species present in the composite materials. The different preparation methods for the monometallic Ni-based cermets led to solids with different resistances to reduction in hydrogen presence, observed by the differences in the areas delimited by the TPR peaks for the different materials. In these samples, the monometallic species that reduced in the temperature range of 410 - 420 °C presented weaker interactions with the support; the converse relation might also be inferred.

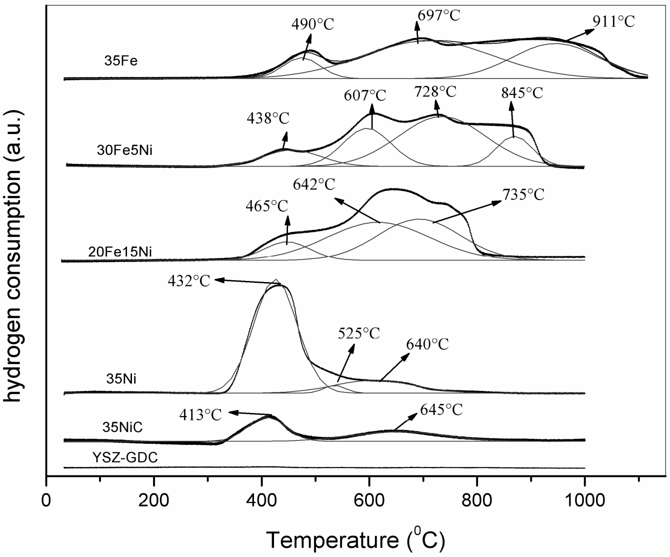
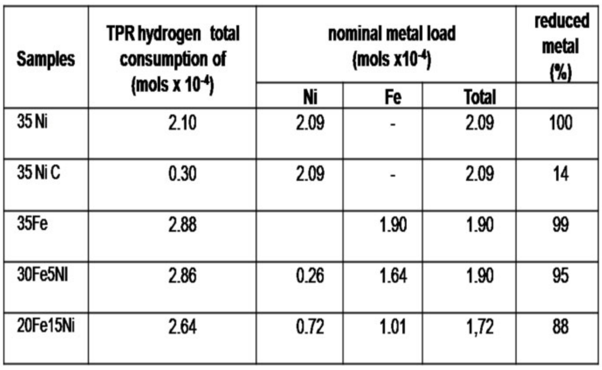


Figure 4: TPR profiles of the studied materials: (—) experimental profile; (—) Gaussian deconvolution of the TPR profiles.

Table 1 presents the quantitative data obtained from the sample TPR analyses. For the monometallic Ni samples, the stoichiometric ratio of 1:1 between H_2 and Ni was considered. For the monometallic Fe sample (35Fe), the stoichiometric relationship between molecular hydrogen and Fe was 3:2. Finally, for the bimetallic samples, the TPR hydrogen consumption was calculated as the sum of the individual consumptions for Ni and Fe species, each proportional to their concentration in the sample. The data indicate that the samples prepared using Pechini method achieved complete reduction of the metal oxides in the presence of hydrogen. In contrast, the 35NiC sample, prepared using the physical mixture method showed a low yield in the reduction of NiO with hydrogen, reducing only 14% of the oxide initially present in the sample.

Table 1: Hydrogen mol consumption obtained from the TPR analyses, the nominal molar load of sample, and the extension of metal reduction.



Samples	TPR hydrogen total consumption of (mols x 10^{-4})	nominal metal load (mols x10^{-4})			reduced metal (%)
		Ni	Fe	Total	
35 Ni	2.10	2.09	-	2.09	100
35 Ni C	0.30	2.09	-	2.09	14
35Fe	2.88		1.90	1.90	99
30Fe5NI	2.86	0.26	1.64	1.90	95
20Fe15Ni	2.64	0.72	1.01	1,72	88

Figure 5 shows the ethanol conversion for the steam reforming reaction at 650 °C for a six hour period of reaction. The results shown indicated that the electro-catalyst remained stable during the six hour period, with average ethanol conversion exceeding 80% for the samples containing Ni and prepared using Pechini method; in contrast, the average ethanol conversions for the 35NiC and 35Fe samples were respectively 43.5% and 54.8%; the average conversions presented standard deviations of less than 5%.

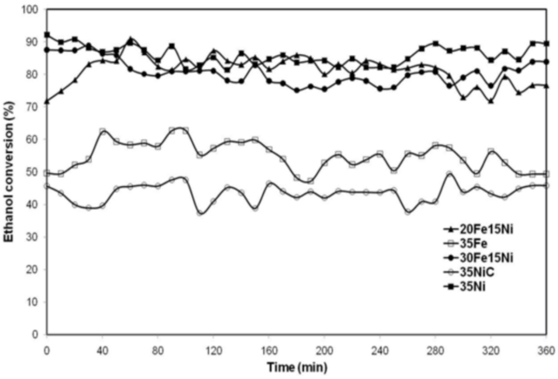


Figure 5: Ethanol conversion versus time on stream for samples prepared.

Figure 6 presents data for carbon deposition during the six hours on stream of the various electro-catalysts studied. The data are presented as carbon mass percentage by the catalyst mass after reduction. The data in Figure 6 strongly suggested that the presence of Fe in the samples significantly decreased the mass of carbon deposited on the electro-catalysts. This might be associated with the lower activity of Fe, compared to Ni, for secondary reactions that led to carbon formation, as observed by Huang et al. [3]. Studying a composite of Ni and Fe supported on ScSZ exposed to ethanol vapor for 24 hours, these authors found that carbon deposits increased as the Ni loading increased.

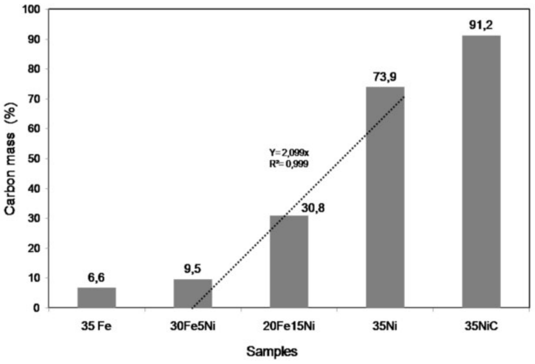


Figure 6: **Carbon deposited on the electro-catalyst for ethanol steam reforming for six hours on stream, at 650 °C. Deposited carbon as percentage of electro-catalyst mass. The straight line correlates carbon formation with Ni contents.**

The preparation method of the electro-catalyst also influenced its activity to catalyze reactions that led to carbon formation. The 35NiC sample prepared by physical mixture formed 17% more carbon than 35Ni sample, prepared using Pechini method. As a final important point, the samples containing Ni and prepared using the Pechini method exhibit a surprisingly linear correlation between the mass of deposited carbon and Ni content in the sample.

4 Conclusion

The Pechini method studied here for the synthesis of Ni-Fe/YSZ-GDC composites was very successfully used to produce powders with crystallographic and morphological characteristics suitable for use in SOFC anodes, whereas materials prepared using the physical method displayed limitations in particle size, reducibility, and hydrogen production.

Ni-Fe/YSZ-GDC composites are highly promising cermets for application as SOFC anode: they have a very high hydrogen yield in ethanol steam reforming reaction with a very low carbon formation. This final remark observation is especially applicable for the composites with low nickel content.

Acknowledgements

The authors gratefully acknowledge grants from the Brazilian Ministry of Science and Technology (MCT). They are especially grateful to Rede PaCOS (Grant 01.06.0901.00) and RECAT (Grant 22.02.0289.00). The authors also acknowledge FAPESB (MAS) and CNPq (RPF) for helpful scholarships.

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