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Ni-YSZ Nanocomposite Synthesis: Mechanochemical vs Novel Sol-Gel Method for Solid Oxide Electrolyzers

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Abstract

Nickel-yttrium stabilized zirconium (Ni-YSZ) nanocomposite were synthesized by to different paths: mechanochemical method and a novel sol-gel method at different temperatures. Preliminary structural/textural results obtained by XRD, BET and SEM analyses showed a typical crystalline cubic structure, with small crystallite size in those nanocomposites synthesized by sol-gel method as well as higher specific surface area and uniform distribution.

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Keywords: sol-gel; mechanochemical; Ni-YSZ nanocomposite; SOEs

1. Introduction

Solid Oxide Electrolyzers (SOE) have been attracted a great deal of attention in the last years due to their high efficiency and environmentally friendly features, which has been stated as a promising energy alternative to those technologies based in fossil fuels.[1, 2] In SOEs the anode is considered as one of the most important part to achieve a high efficiency.[3] In this sense, the materials for anode manufacturing should have properties such as high electronic conductivity, thermal expansion compatibility, as well as a determined microstructure to enhance the electrochemical reactions which occurs in the Three-Phase Boundary (TPB).[4] Nickel-yttrium stabilized zirconium (Ni-YSZ) composite is one the most studied materials for anode manufacturing due to its mechanical properties, low cost

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synthesis as well as its reliability.[5] Recently, scientific community has been focused in decrease the operational temperature from the typical 1000 °C to an intermediate value between 600-850°C, which would increase the cell durability and reduce total costs, being possible to compete with the well established technologies. However, YSZ shows a low oxygen ion conductivity at lower temperatures, affecting to the electrochemical activity of the cell. It was proven by fundamental studies that increasing the TPB surface, the electrochemical activity of Ni-YSZ materials can be enhanced. This fact can be achieved by the improvement of the anode microstructure which is directly related with the nickel distribution as well as the control of the nanoparticle sizes.[6, 7]. In the past years several synthesis approaches were reported, being the most common the mechanical mixture of the nickel source and the YSZ powder.[8] However, initial results showed the production of large crystalline nanoparticles and low homogeneity in the nickel distribution. Other methods, such as combustion, spray pyrolysis, tape casting, chemical synthesis, solid state reaction as well as plasma synthesis were recently described,[3] providing a uniform distribution of nickel nanoparticles through the YSZ material. Sol-gel strategy for anode materials is considering a promising alternative due to it can achieve not only a homogeneous distribution of the components but also reduced nanoparticles size.[9] According to this, in this work we present the synthesis of Ni-YSZ nanocomposite by a new sol-gel method. The structural/textural properties of the prepared materials were then studied by different techniques such as XRD, BET and electronic microscopy. Ni-YSZ material was also synthesized by a typical mechanochemical method and the results were compared.

2. Materials and Methods

2.1. Sol-Gel Synthesis Method

The synthesis of the YSZ and Ni-YSZ were carried out in a two-step protocol based on the neutral templating method by using small, non-surfactant templates, as triethanolamine (TEA) to direct the polycondensation of inorganic species.[10] Specific amounts of metal precursors were dissolved in deionized water, using magnetic stirring, to obtain the precursor solution. Then TEA was added into the solution and stirred at 45 °C during 30 min, followed by the addition of tetraethylammonium hydroxide (TEAOH), and stirred overnight to obtain a homogeneous gel.

The formed gel was then dried by solvent exchange with ethanol several times and stirred at room temperature. Organic template was removed by calcination at different temperatures (700, 800, 900 °C) during 6h in air in order to obtain YSZ and Ni-YSZ powders.

2.2. Mechanochemical Synthesis Method

In order to synthesize Ni-YSZ material by mechanochemical method, two metal precursors were used in the synthesis. NiO and Ni(NO₃)₂ were used as nickel source and mixed separately with commercial YSZ in a planetary ball mill (Fritsch, Pulverisette 6). Different milling conditions were carried out. Both Ni precursor materials and commercial YSZ were obtained from Sigma-Aldrich. Different combination of theoretical weight ratio and milling conditions were utilized to obtain optimal synthesis conditions. After milling, the powder was then calcined at different temperatures during 6 h in air, with a heating rate of 10 °C/min to obtain the oxide phase

The nanocomposites were named according to the utilized nickel source (*NiO*: Ni₁; *Ni(NO₃)₂*: Ni₂), synthesis method (*BM*: ball-mill; *SG*: sol-gel) and calcination temperature (700, 800, 900 °C) For example, Ni₂-YSZ-SG800 corresponds with the material synthesized by sol-gel method at 800 °C using Ni(NO₃)₂ as nickel precursor.

2.3. Characterization

Synthesized materials were structurally characterized by XRD analysis using a Bruker D8 Advance powder diffractometer, operating with Ge-monochromated Cu Kα radiation and a LynxEye linear detector. The data were collected over the angular range of 5-85 2θ (°). Scherrer equation was used to determine the crystallite particle sizes. Specific surface area (BET) was calculated by nitrogen isotherms using a Gemini VII (Micromeritics) analyzer, operated with an evacuation rate of 100 mmHg/min (6 min) and equilibration time of 5 s. Samples were previously

degassed at 200 °C for 4 h. Particles morphology was studied by Scanning Electron Microscopy (SEM) using a Quanta microscope (3D FEG, FEI).

3. Results and Discussion

A new sol-gel method was carried out for the synthesis of Ni-YSZ nanocomposites. The protocol entails the utilization of non-surfactant templates, avoiding any thermal step/aging during the synthesis. After obtain the dry gel, the material was calcined a different temperatures to obtain the final nanocomposite. The synthesis of Ni-YSZ was also carried out by a solvent-free mechanochemical method using two different nickel sources in a theoretical weight ratio of Ni:YSZ 1:1 respectively. The different synthesis conditions are summarized in Table 1.

Table 1. Synthesis conditions of Ni-YSZ.

Nickel precursor	Theoretical weight ratio (Ni:YSZ)	Milling conditions (rpm:min)	Temperature of calcination (°C)
Ni ₁ -YSZ-BM	1:1	350:15	
Ni ₂ -YSZ-BM	1:1	200:60	700/800/900
Ni ₁ -YSZ-SG	1:1	-	

In order to study the structural/textural properties of the synthesized materials, different characterization techniques were carried out.

Crystalline phase of YSZ and Ni-YSZ nanocomposites were studied by XRD analysis. Figure 1a) illustrates the patterns of anode materials prepared by BM method using different nickel sources. Similar patterns peaks were observed at 700, 800 and 900 °C. The patterns correspond with cubic NiO and cubic YSZ, which are the typical phases for their utilization as anode/electrode materials in solid oxide cells.[11] XRD of sol-gel synthesized materials (Figure 1b) shows broader peaks to those obtained by ball-mill. Crystallite size of the different prepared composites was measured using Debye-Scherrer formula and the results are shown in Table 2.

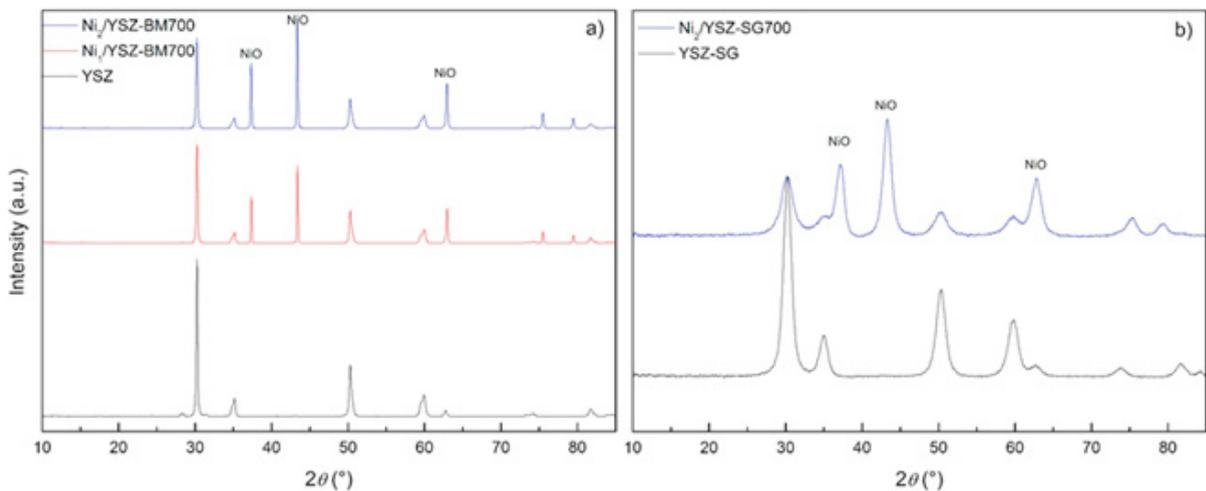


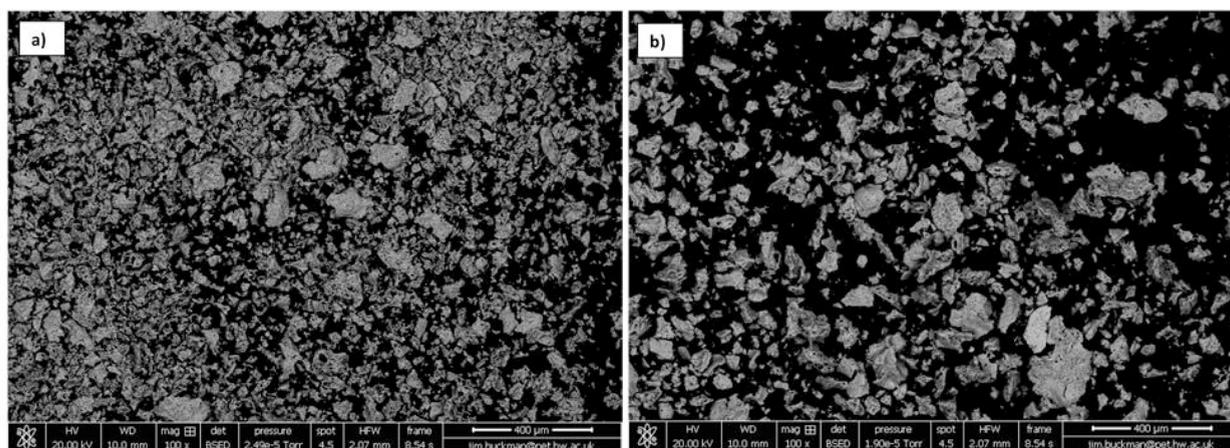
Figure 1. XRD spectra of YSZ composites: a) by ball-mill; b) by sol-gel method

Table 2. Crystallite size of Ni-YSZ nanocomposites.

Temperature	700 °C		800 °C		900 °C	
Particle size	NiO (nm)	YSZ (nm)	NiO (nm)	YSZ (nm)	NiO (nm)	YSZ (nm)
Ni ₁ /YSZ-BM	46.94	61.83	49.46	74.36	52.66	96.18
Ni ₂ /YSZ-BM	37.22	66.49	41.18	67.34	43.28	71.91
Ni ₂ /YSZ-SG	7.79	12.98	11.66	16.43	23.67	37.75
YSZ-SG	-	15.89	-	24.34	-	47.68
Commercial YSZ	-	79.39	-	-	-	-

By ball-mill method, composites prepared using Ni(NO₃)₂ as nickel precursor shows a relative smaller value compared with NiO materials. This could be due to the salt decomposition to nickel oxide during calcination, which can affect to the particle aggregation.[12] On the other hand, Ni-YSZ materials synthesized by sol-gel method, the values are several times smaller compared with BM materials in all cases. This is could be due to the utilization of an initial template, which avoids the sintering process at medium/high temperatures (600-900 °C).

N₂ isotherms were carried out to study structural properties of the synthesized composites. Initial results show a high specific surface area for materials obtained by sol-gel method, with values up to 43 m²/g (Ni₂-YSZ-SG700) compared with ball-milled materials (5 m²/g and 12.43 m²/g for Ni₁/YSZ-BM and Ni₂/YSZ-BM respectively). The morphology of the Ni/YSZ nanocomposite is shown in Figure 2.

Figure 2 SEM micrographs of: a) Ni₂-YSZ-SG900 and b) Ni₂-YSZ-BM900

4. Conclusions

Ni-YSZ nanocomposites were synthesized by a novel sol-gel protocol, avoiding the utilization of heat/aging steps. As comparative, Ni-YSZ nanocomposite was also prepared by a mechanochemical method. Results obtained from characterization analyses showed a typical cubic structure with an average crystallite sized smaller in sol-gel synthesized materials. Moreover these nanocomposites showed the highest surface area and homogeneous distribution

of their components. These results indicates that the materials prepared by sol-gel method show a promising properties for their utilization as anode in SOEs, which is currently under development in our laboratory.

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