Influence of organic solvent on solvothermal synthesis of samaria and gadolinia doped ceria – nickel oxide composites

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Abstract. The synthesis and ceramic processing of samaria and gadolinia doped ceria - nickel oxide composites, mainly applied as Solid Oxide Fuel Cell anodes, were studied in this work. Powders with composition $Ce_{0.8}(SmGd)_{0.2}O_{1,9}$/NiO and mass ratio of 40/60%, were synthesized by hydroxide coprecipitation with CTAB surfactant, followed by solvothermal treatment in n-butanol, ethanol and n-propanol at 150 ºC for 16 hours, calcination at 600°C for 1 hour and milling. Sintering of compacted samples was performed at 1300°C for 1 hour. The powders were analyzed by X-ray diffraction, scanning electron microscopy, nitrogen adsorption method (BET), laser beam scattering (Cilas) and TG/DTA. The ceramics were analyzed by scanning electron microscopy, EDS, XRD and density measurements by Archimedes method. The results showed that the powders have a high specific surface area (42 - 85 m^2/g). The ceramic characterizations showed a high chemical homogeneity and density value of 99% TD for powders treated with ethanol and propanol.

Introduction

The (CeO_2) based ceramics have been widely studied due to its high ionic conductivity allowing their use as Solid Oxide Fuel Cell electrolyte. The dopants that provide highest improvement in the ionic conductivity are the trivalents rare earths samaria and gadolinia. The anodic materials that present high chemical, physical compatibility and highest electronic conductivity with ceria based electrolytes are the cermets compounds containing metallic nickel and the same electrolyte material [1,2]. Metallic nickel can be formed by reduction in hydrogen atmosphere from the nickel oxide produced by coprecipitation with the gadolinia and samaria doped ceria (GSDC) [3]. The anodic composite performance depends on the powder characteristics such as particle size, surface area, and chemical homogeneity, as well as on ceramic microstructure, including triple phase boundaries (TPB) and percolation chains [1-3]. It is well known that these properties can be adjusted during the powder synthesis and gel precipitation is a usual employed method. The association with solvothermal technique was recently introduced to allow the preparation of crystalline nanopowders at low temperatures [4]. This process involves the use of an organic solvent in an autoclave under autogenous pressure of 10-30 atm generated by temperatures from 100 to 250ºC. These conditions promote the growth of the particles in preferred directions, making possible the formation of particulate forms of nanocubes, nanorods, nanotubes and nanoplates[5]. The shape of the particles can also be changed with the employment of a surfactant in precipitation, which operates in the nucleation, particle growth, coagulation and flocculation[6]. For this purpose parameters like pH of precursors solution, reaction temperature and time, solute concentration and type of solvent have to be controlled[5,6]. In this work samaria and gadolinia doped ceria - nickel oxide powders have been synthesized by coprecipitation, in the presence of CTAB (hexadecyltrimethylammonium bromide) surfactant, followed by solvothermal treatment.

Materials and Methods

Chlorides of cerium, samarium, gadolinium and nickel, obtained by respective oxide dissolution, (purity > 99,9%, Aldrich) were used as starting materials in the $Ce_{0,8}(SmGd)_{0,2}O_{1,9}$ / NiO synthesis, with mass ratio 40/60%. Precipitation synthesis was performed by heating the solution containing the metallic ions (Me) and CTAB, with ratio Me/CTAB = 2, dropwised to a stirred ammonia solution 7.0M at 98 ºC. Ni^{2+} ions concentration was fixed at 0.1M to avoid nickel loss. The final pH was 7 and the supernatant was light blue. The obtained gels were submitted to washing with water to remove the chloride ions, and then solvothermically treated at 150 ºC for 16 hours in butanol, ethanol or propanol. The resulting powders were divided in two portions: the first one was oven-dried at 80ºC for 24 hours and then ball-milled for 16 hours. The second fraction was submitted to calcination at 600ºC for 1 hour, ball milling in ethanol and oven-drying at 80ºC for 24 hours. For comparison purposes, two others experiment were performed: (a) without CTAB and solvothermal synthesis and (b) without CTAB and with solvothermal treatment in butanol. The sample codes are explained in Table 1. The addition of the code C600 identifies calcined samples and the code 1300 the sintered samples.

Table 1. Experiments codes according to synthesis procedure.

Sample code	CTAB	Azeotropic Distillation	Solvothermal Treatment
GSDC/NiO E	YES	NO	Ethanol
GSDC/NiO P	YES	NO	Propanol
GSDC/NiO D	NO	YES	NO
GSDC/NiO B	NO	NO	Butanol
GSDC/NiO B2	YES	NO	Butanol

The resulting powders were pressed by uniaxial compaction at 100MPa in a metallic matrix. The green pressed pellets were sintered in air at 1300ºC for 1 hour using an electrical box furnace (*Lindberg/Blue M*). The powders were characterized by X-ray diffraction (*Rigaku, Multiflex*), scanning electron microscopy (*Philips, XL30*), agglomerate size distribution by laser scattering (*CILAS, 1064*), thermal analysis (TG/DTA) (*Setaram Labsys Instrumentation, TG-DTA/DSC*) and specific surface area by gas adsorption (B.E.T.) (*Quantachrome, Nova 1200*). Ceramic sinterability was evaluated by density measurements using Archimedes method and the ceramic pellets were characterized by X-ray diffraction, scanning electron microscopy and EDS (*Hitachi, TM 3000*).

Results and Discussions

Figure 1 shows XRD patterns of ceria-nickel based powder after solvothermal treatment and calcination. After solvothermal synthesis powders are formed by ceria fluorite phases structure (JCPDS-34-394) and nickel hydroxide (JCPDS 14-117). The calcination step keeps ceria fluorite phase and provides the formation of monoclinic nickel oxide structure (JCPDS 71-1179).

The particle size distribution curves presented in Fig. 2 show the similar distribution and mean agglomerate size of 1 – 1.5 μm for the not calcined powders and 1.5 – 2.0 μm for the calcined powders. It is worth noting just the GSDC/NiO-P higher agglomerate average size of 5.1 μm and different distribution curve.

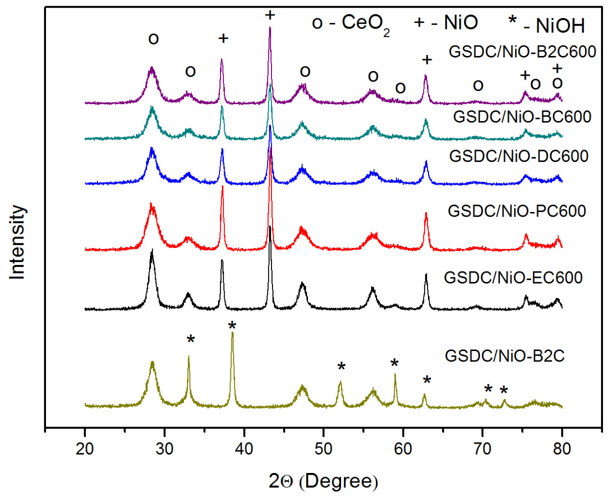


Figure 1. X-ray diffraction patterns of $Ce_{0,8}(SmGd)_{0,2}O_{1,9}$ / NiO synthesized powders.

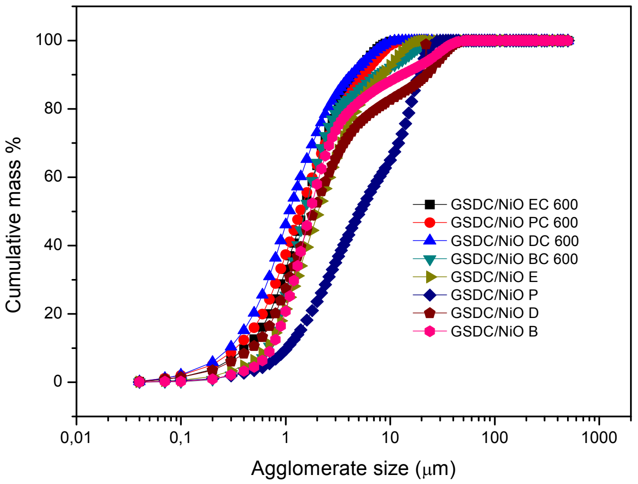


Figure 2. Agglomerate size distribution curves of $Ce_{0.8}(SmGd)_{0.2}O_{1.9}$ /NiO synthesized powders.

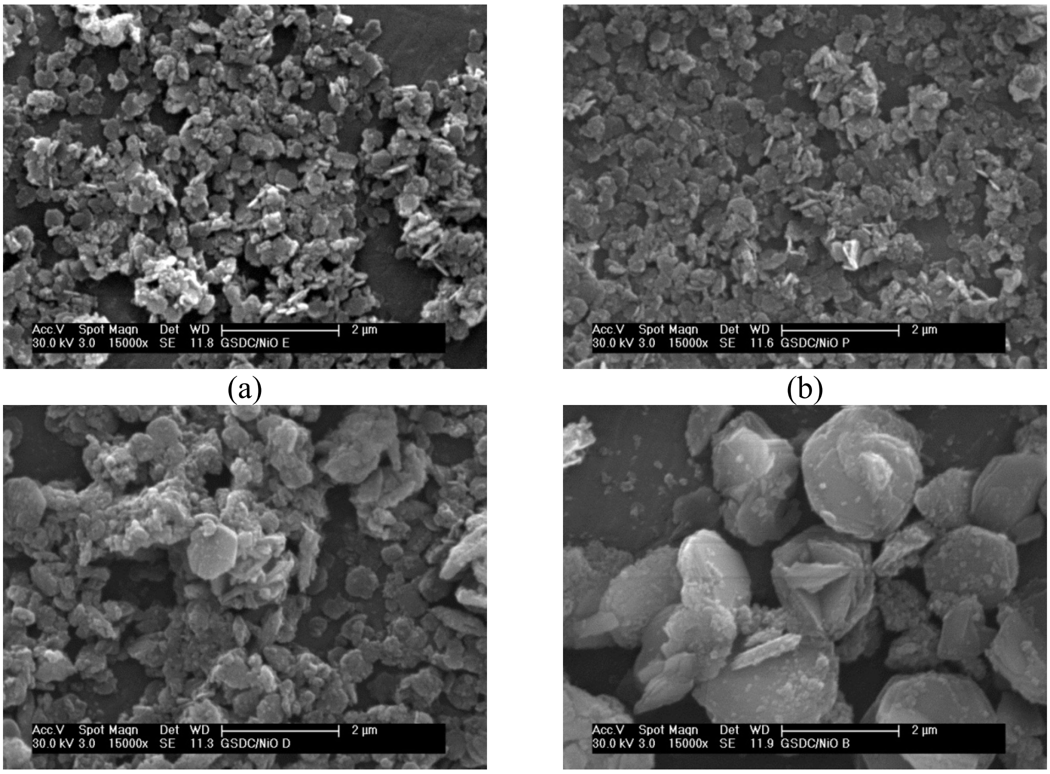
Specific surface area values of prepared powders are presented in Table 2. It can be observed that all powders have high reactivity, around 70 - 97 $m^2.g^{-1}$ for not calcined powders, and the calcination step decreases this reactivity. Higher specific surface area was found for the powders synthesized by solvothermal treatment in propanol without calcinations (GSDC/NiO-P sample). Among calcined powders GSDC/NiO-PC600 has the higher surface area.

Table 2. Specific surface area values of $Ce_{0.8}(SmGd)_{0.2}O_{1.9}$ /NiO synthesized powders.

Sample code	Specific surface area (m^2/g)	Sample code	Specific surface area (m^2/g)
GSDC/NiO-E	72.4	GSDC/NiO-EC600	42.6
GSDC/NiO-P	97.5	GSDC/NiO-PC600	72.4
GSDC/NiO-D	81.6	GSDC/NiO-DC600	67.3
GSDC/NiO-B	85.4	GSDC/NiO-BC600	71.9
GSDC/NiO-B2	78.1	GSDC/NiO-B2 C600	74.3

SEM micrographs (Fig.3 and 4), show the solvothermal treatment influence on the agglomerate size and morphology. It can be seen that GSDC/NiO-E and GSDC/NiO-P powders (Fig.3 a. and b.) are formed by smaller plates and are less agglomerated than GSDC/NiO-D GSDC/NiO-B powders (Fig.3 c. and d.). As seen in the Table 3, GSDC/NiO-E and GSDC/NiO-P powders after calcination and pressing, produce ceramics with higher densities, probably due to the dispersion promoted by CTAB and/or the complete formation of nickel oxide after calcination. (Fig. 4). Considering the theoretical composite density of 6.9 $g.cm^{-3}$, the ceramic GSDC/NiO – PC600-1300 reached 99% of theoretical density.

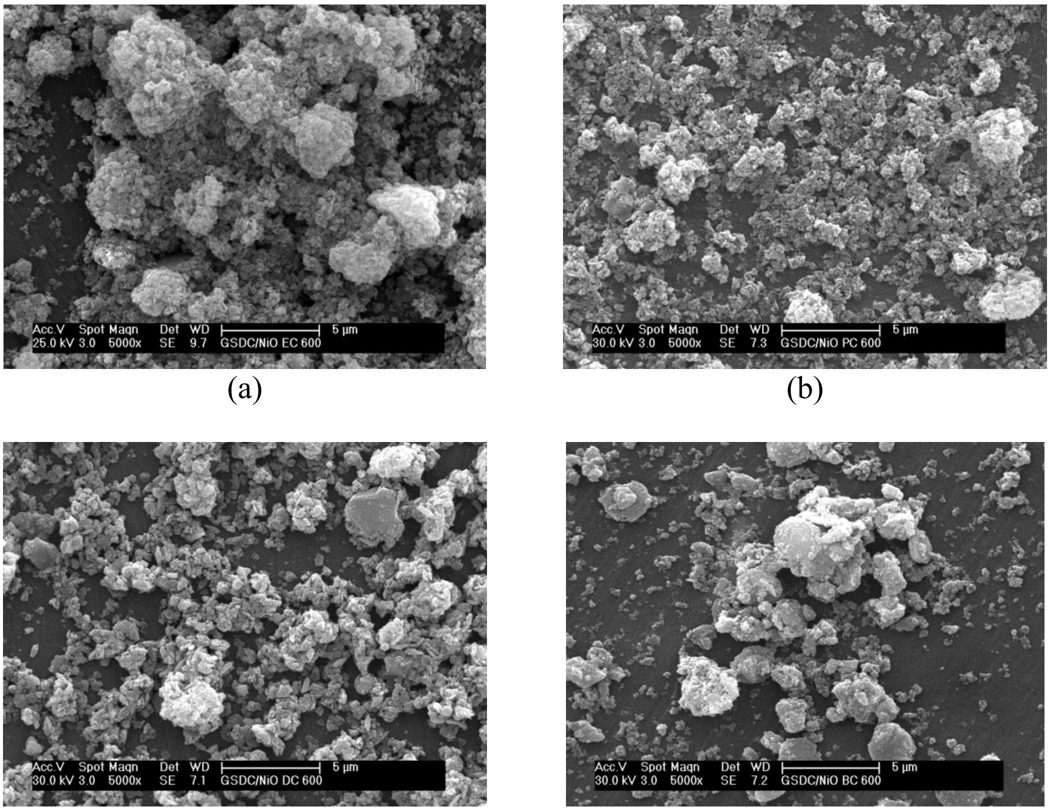
The TG/DTA results of the thermal decomposition process of synthesized samples after precipitation, solvothermal treatment in butanol and drying , as a function of CTAB addition , are shown in Fig.5. The weight loss around 15% is due to the remain removal of free water until 200ºC and after that, structural OH^- groups of hydrated oxides. Endothermic peaks are produced by the weight loss up to 300ºC. Exothermic peak corresponds to the improvement of oxide crystallization and the oxidation of Ce^{3+}[6]. The samples synthesized with and without CTAB presented the same behavior, although the CTAB use causes slight faster decomposition and smaller weight loss.



(a) (b)

(c) (d)

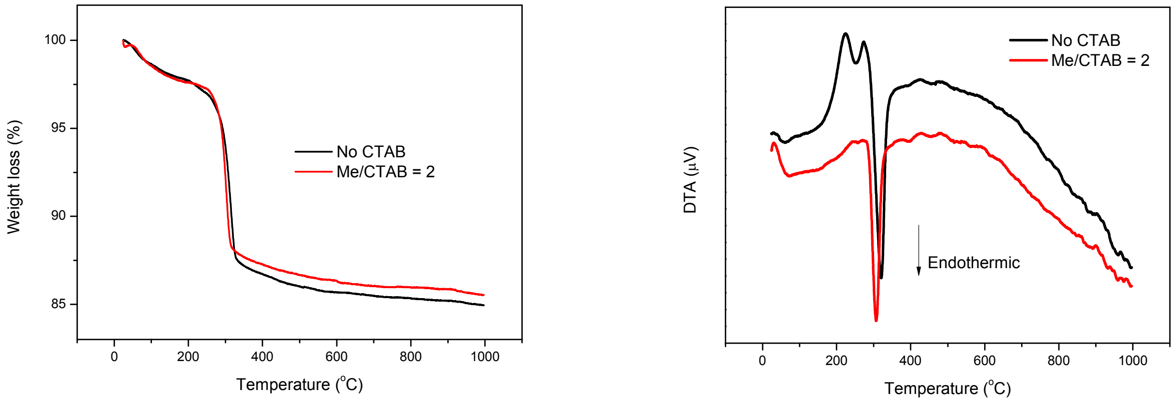
Figure 3. SEM micrographs of $Ce_{0.8}(SmGd)_{0.2}O_{1.9}$ / NiO synthesized powders: (a)GSDC/NiO-E, (b)GSDC/NiO-P, (c)GSDC/NiO-D and (d)GSDC/NiO-B.



(a) (b)

(c) (d)

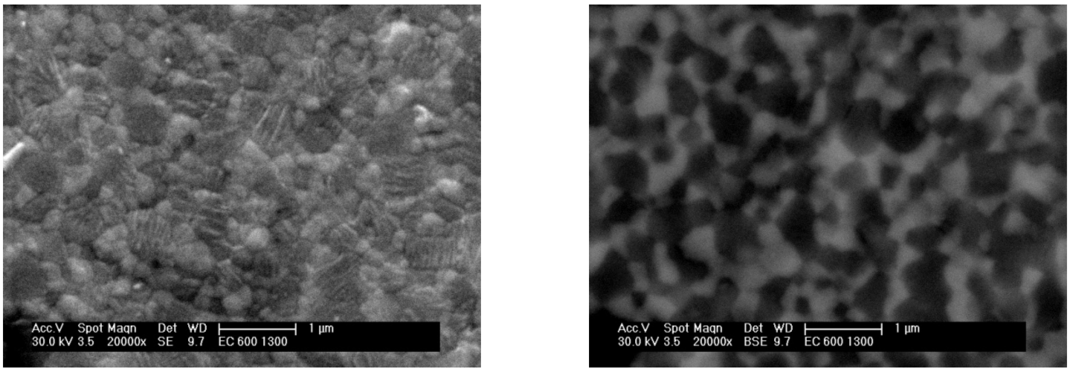
Figure 4. SEM micrographs of $Ce_{0.8}(SmGd)_{0.2}O_{1.9}$ / NiO calcined powders: (a)GSDC/NiO-EC600, (b)GSDC/NiO-PC600, (c)GSDC/NiO-DC600 and (d)GSDC/NiO-BC600



(a) (b)

Figure 5. (a) TG and (b) DTA analysis of $Ce_{0.8}(SmGd)_{0.2}O_{1.9}$ /NiO powders synthesized by coprecipitation, solvothermal treatment in butanol and drying, as a function of CTAB presence.

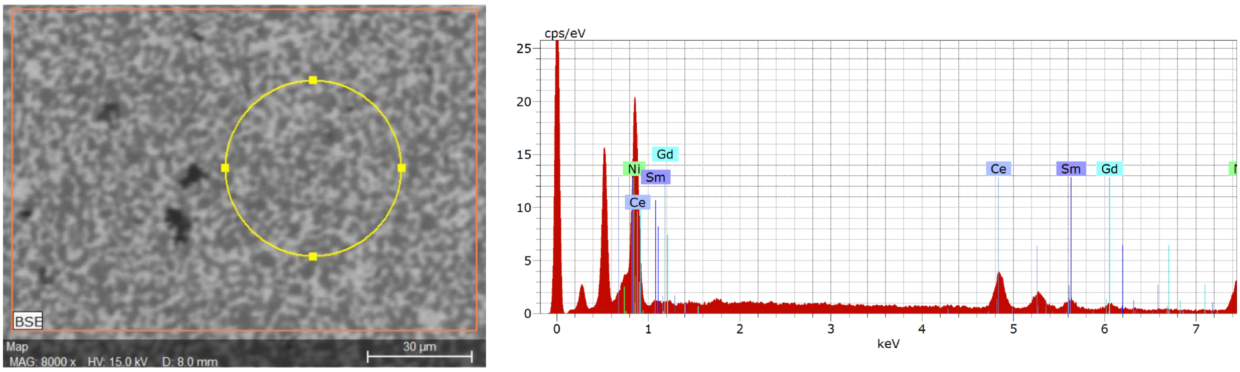
The doped ceria and nickel oxide ceramics homogeneity verification was made by polished and thermally etched GSDC/NiO-EC600 samples using scanning electron microscopy with secondary (SE) and backscattered electrons (BSE) detection, and the micrographs are shown in Fig.6. This images present grain sizes of approximately 100nm and homogeneous distribution of constituent components. NiO grains appear darker and larger than the $Ce_{0,8}(SmGd)_{0,2}O_{1,9}$ grains.



(a) (b)

Figure 6. SEM micrographs of $Ce_{0.8}(SmGd)_{0.2}O_{1.9}$ / NiO ceramics: (a) (SE)GSDC/NiO-EC600-1300, (b) (BSE) GSDC/NiO-EC600-1300.

In order to verify the elements distribution in the microstructure of GSDC/NiO-PC600-1300 samples, SEM-EDS analysis was performed on the yellow circled area shown in Fig.7a. This analysis indicates the presence of all precipitated elements in this area. The estimated EDS chemical analysis (semi quantitative) indicates that the desired stoichiometry was reached.



(a) (b)

Figure 7. SEM-EDS results for the GSDC/NiO-EC600-1300 ceramics: (a) SEM micrograph, (b) EDS spectrum of the yellow circled area (a).

The X-ray diffraction patterns of $Ce_{0,8}(SmGd)_{0,2}O_{1,9}$ / NiO ceramics presented in Fig.8, show the formation of crystalline ceria and nickel oxide.

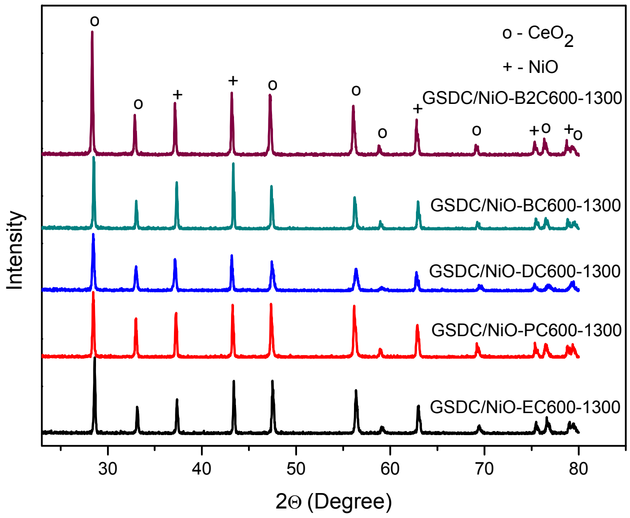


Figure 8. X-ray diffraction patterns of $Ce_{0,8}(SmGd)_{0,2}O_{1,9}$ / NiO ceramics.

Table 3. Density of the $Ce_{0.8}(SmGd)_{0.2}O_{1.9}$/NiO ceramic pellets.

Sample code	**Sintered density ceramic (g.cm^{-3})**	
	Without calcination	**Calcined at 600 °C**
GSDC/NiO - E	6.35	6.79
GSDC/NiO - P	5.91	6.83
GSDC/NiO - D	5.95	6.51
GSDC/NiO - B	4.87	5.01
GSDC/NiO – B2	4.72	5.53

Conclusions

Solvothermal treatment with organic solvents of ceria-nickel oxide based gels coprecipitated in the presence of CTAB surfactant provides a homogeneous composite formation. This is an important factor to materials applied as Fuel Cells Anodes, considering that this component depends on a high ionic and electronic conductivity, and therefore on the metallic phase percolation. The use of CTAB surfactant in $Ce_{0,8}(SmGd)_{0,2}O_{1,9}$/NiO coprecipitation route synthesis, contributes to the increase of specific surface area of powders, and also the improvement of ceramic density and microstructure, especially for powders treated with propanol. The calcination step is necessary in order to the complete nickel oxide formation during synthesis.

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