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Microwave-Assisted Combustion Synthesis of Nanocrystalline $NdCoO_3$ Cathode Material for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs) Application

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Abstract

A nanocrystalline $NdCoO_3$ was synthesized by a simple and effective microwave irradiation using a domestic microwave oven with a microwave irradiation time of 50 minutes using aspartic acid as fuel. This process remarkably reduced the synthesis time and $NdCoO_3$ was produced relatively quickly for the first time. The formation of a single phase nanocrystalline $NdCoO_3$ powder was confirmed by X-ray diffraction (XRD) studies. The particles size was confirmed by XRD line broadening analysis using the Scherrer equation. The particle distribution and structural morphology analysis of the synthesized product was observed by SEM. The synthesized materials showed reasonable electrical conductivity. These results indicate that microwave assisted combustion method is a promising method to prepare nanocrystalline $NdCoO_3$ cathode material for solid oxide fuel cell application.

Keywords: *Aspartic acid; Intermediate Temperature Solid Oxide Fuel Cells; Microwave- assisted combustion method; $NdCoO_3$; Perovskite oxide.*

1. INTRODUCTION

The solid oxide fuel cell (SOFC) has attracted much attention due to their high energy conversion efficiency, low pollution and ability to use hydrocarbon fuels. The electrodes are one of the main components in the SOFC, and the use of alternative materials with improved performance. It is required for a reduction in the operating temperature from 500-800 °C (Lee and Manthiram, 2005). The cathode material in the SOFC, at reduced operating temperature has to meet the following requirements: high electrical conductivity, thermal and chemical compatibility with the electrolyte and high catalytic activity for oxygen reduction. Cobalt containing perovskite oxides such as $LaCoO_3$, tend to exhibit higher ionic conductivity due to a greater concentration of oxide vacancies than other perovskite cathode materials.

Nanocrystalline powders have many excellent chararecters suited for various applications such as ceramics, gas sensor, rechargeable ceramic batteries, SOFC, etc. In addition, they can significantly enhance sintering rates, decrease sintering temperature and improve optical, electric and magnetic properties compared to the micrometer size powders (Zhou and Rahaman, 1993; Subbarao and Maiti, 1984).

In this work, we have attempted the synthesis of $NdCoO_3$ nanocrystalline powder by a domestic microwave assisted combustion synthesis process. The microwave assisted combustion synthesis process is a novel method of synthesis and a very rapidly developing area of research (Rao *et al.* 1989). In a microwave oven, heat is generated internally within the sample itself by interaction of microwaves with the material instead of originating from an external heating source as in conventional oven. Microwave synthesis is generally considered fast and very energy efficient. Temperature measurement in a microwave oven is not straightforward, but it has been reported that reactions occur at lower temperatures in a much

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shorter time in microwave synthesis than in conventional combustion synthesis method (Yan *et al.* 1997).Microwave synthesis also has products with good phase purity and degree of crystallinity(Aylon*et al.* 2000; Kannan and Jasra, 2000) and nanoscale particles (Palchick *et al*. 2000;). With larger surface area (Palchick *et al*. 2000; Fetter *et al.* 1996; Du *et al.* 1997; Ranjan Kumar *et al.* 2001).

2. EXPERIMENTAL PROCEDURE

The synthesis of nano crystalline powders $NdCoO_3$ by using $Nd(NO_3)_3$ and $Co(NO_3)_3$ as starting materials in a stoichiometric ratio of 1:1. The aspartic acid is used as fuel. The stochiometric amounts of $Nd(NO_3)_3$ and $Co(NO_3)_3$ were dissolved indistilled water, and the as partic acid solution is added into this solution. This solution becomes transferent pink colour and it is kept at constant heating at 80 °C to obtain the foamy powders of $NdCoO_3$ is shown in the flowchart Fig.1 for calcinations, the foamy powder was carried out in a domestic microwave oven with a maximum power of 900W and magnetron frequency of 2.45 GHz.

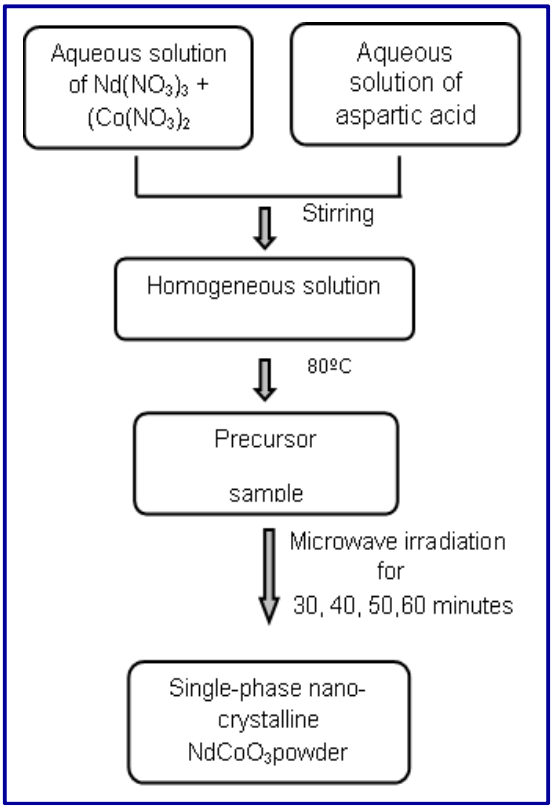

Fig. 1: Flow chart of microwave assisted combustion synthesis of $NdCoO_3$

The experiment was performed based on the microwave irradiation time duration at about 30, 45 and 60 minutes to optimize the synthesized nanocrystalline powders. The synthesis of nanocrystalline powder was calcined at the microwave irradiation time of 60 min. The calcined powders were then mixed with 3% polyvinyl alcohol and pressed into pellets with a diameter of 13 mm under uniaxial pressure (200 MPa). Dense samples were obtained by sintering the pellets at 1073 K for 5 hin air with heating and cooling rate of 5 ºC/min. Rectangular bars of approximate dimensions of 7 x 3 x 1 mm^3 were cut from the sintered pellets for the electrical conductivity, and thermal expansion coefficient (TEC) measurements. The bars had a density in excess of 95% of the theoretical value as determined from the Archimedes method.

3. CHARACTERIZATION

X-ray powder diffraction patterns were obtained using Philips diffractometer and Cu Kα radiation The particle size was calculated from XRD line broadening by using Scherrerequation. Scanningelectron microscopy (SEM) micrographs were taken with JEOL JSM-840. The calcined fine powders were examined by transmission electron microscope (TEM);JEOL (Model: 1200EX). The specific surface areas of the powders were measured by the Brunuer-Emmet-Teller (BET) method (N_2 adsorption). Thermal expansion coefficient was obtained using Dilatometer from 50-700°C with a heating/cooling rate of 10 °C/min. The densities of sintered bar was measured by the Archimedes liquid displacement technique using distilled water as the medium. The electrical conductivity was measured by a four probe D.C method in the temperature range 200-700 °C in air.

4. RESULTS & DISCUSSION

4.1 X-ray diffraction studies

XRD analysis was performed on the prepared $NdCoO_3$ nanocrystalline powders obtained at different microwave irradiation times as shown in **Fig.2.** Irradiation at 30 minutes, significant peaks which represent $NdCoO_3$ began to appear. The peaks became sharper with increasing the irradiation time to 50 minutes, indicating the formation of phase pure $NdCoO_3$. With further increasing the irradiation time to 60 minutes. There was no improvement in the peaks intensity. It revealed that the optimum irradiation time for the formation of well defined crystalline $NdCoO_3$ powder is 50 minutes. The lattice constant (a=5.3360 , b=5.3509 , and c=7.5546) of the

product formed by microwave assisted combustion method is identical with the sample prepared by conventional solid state method. No detectable impurity peak was observed in the X-ray diffraction pattern.

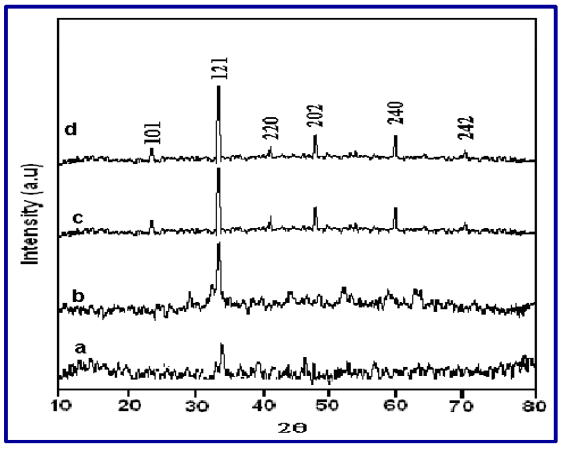

Fig.2: XRD patterns of the $NdCoO_3$ synthesized by using microwave irradiation at different time duration (a) 30 min (b) 40 min (c) 50 min (d) 60 min

4.2 Particle size analysis

The average particle size of the prepared $NdCoO_3$ was calculated from X-ray line broadening analysis using Scherrer equation [16].

$$D=\frac{0.9\lambda}{\beta\cos\theta}$$

where D is the average particle size, λ is the wave length of Cu Kα radiation, β is the width (in radian) of the X-ray diffraction peak at half of its maximum intensity, and θ is the Bragg diffraction angle of the line. The average crystallite size values of $NdCoO_3$nanopowder obtained at microwave irradiation time of 50 min and it was 24 nm. The smaller average crystallite size (nanoparticles) was achieved by using microwave assisted combustion method compared to conventional solid state reaction method (Yan *et al*.1997). Larger size of particles could be obtained by sintering the pellets due to the nucleation of smaller particles at high temperature (800 °C).

4.3. SEM analysis

Fig.3a shows the microstructure of $NdCoO_3$ powder obtained at the microwave irradiation time of 50 minutes. It can be seen that the prepared powder contained nanoparticles and the size of the particles was <25 nm.

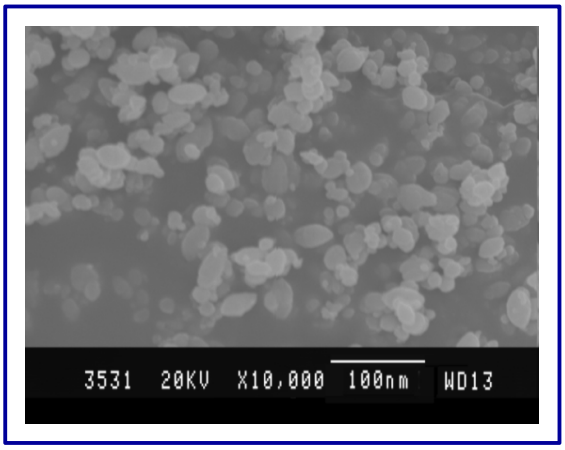

Fig.3a: SEM image for calcinations

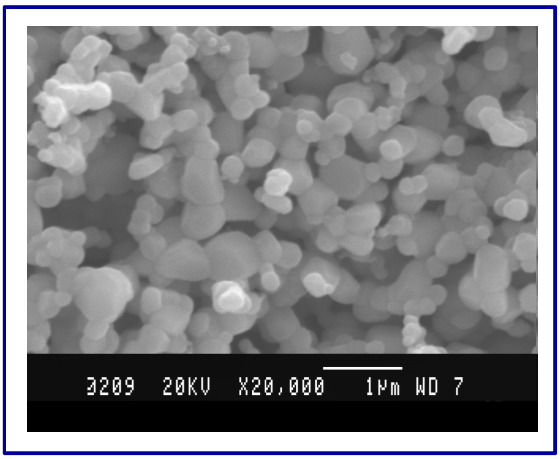

Fig. 3b: SEM image for sintering $NdCoO_3$

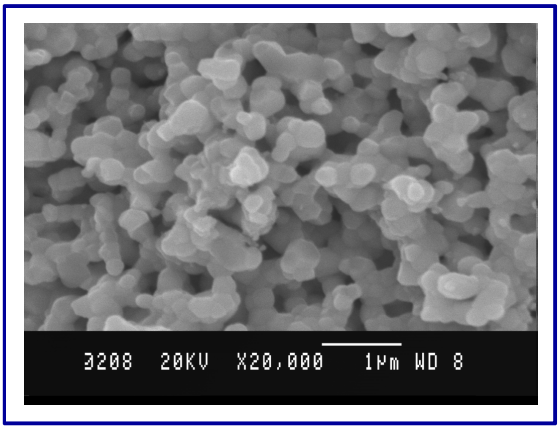

Fig. 3c: Cross sectional view of the sintered pellet of $NdCoO_3$

Fig 3b shows the microstructure of $NdCoO_3$ pellet sintered at 800 °C for 5h. The microstructure showed that the sintered specimen composed of agglomerated grains of different sizes and shapes. From the porosity data of $NdCoO_3$ (Table 4.2), it can be seen that the porosity of $NdCoO_3$ was found to be decreased with increase in temperature and it was found to be 30.08 % for the sample sintered at 800 °C. Beyond this temperature (850 °C), the porosity was decreased to 18.19%. A fine particle size and the porosity of ~30% is required for a cathode to promote the mass- transfer of the oxidant gas effectively. The $NdCoO_3$ sintered at 800°Ccan produce a porous cathode for IT-SOFC application. **Fig.3c** shows the cross sectional view of the sintered pellet of $NdCoO_3$

4.4 TEM Studies

The morphology and size of the $NdCoO_3$ particles were observed by TEM analysis as shown in **Fig.4.** The particle size of $NdCoO_3$ was ~23nm. It showed that the particle size was reduced and the aggregates formation was limited and showed the presence of compact nanocrystallite. The calculated particle size is good agreement with those obtained from XRD value.

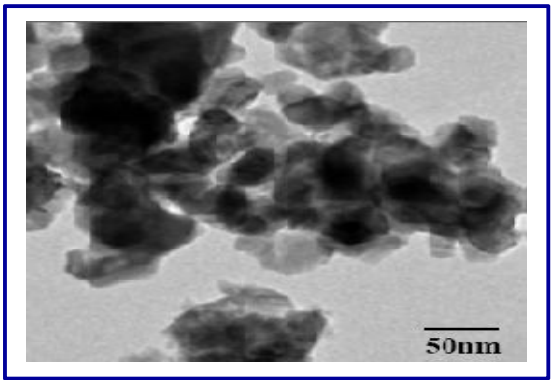

Fig. 4: TEM photograph of $NdCoO_3$

4.5. BET Surface area analysis

The BET surface area of $NdCoO_3$ cathode material is $25m^2/g$. The surface area of $NdCoO_3$ cathode powder revealed the fine nanoparticle nature of the combustion product. The surface area of $NdCoO_3$ obtained by microwave assisted combustion method is higher than the same obtained by other reported methods.

4.6 Thermal expansion

The linear thermal expansion coefficient of $NdCoO_3$ was obtained on heating from 50-700°C in air **Fig.4.** The average thermal expansion value was calculated from its slope of the curve as shown in **Fig.5** and its value is 25.4 x 10^{-6} $°C^{-1}$. The thermal expansion coefficient of nanocrystalline $NdCoO_3$ was lower than the same obtained by solid state reaction method (Lee and Manthiram, 2005) due to its particle nature. The thermal expansion coefficient almost increased linearly with temperature from 50-700ºC is due to loss of oxide ion from the lattice (Subbarao and Maiti, 1984; Rao *et al.* 1989)**.** The larger thermal expansion coefficient value of $NdCoO_3$ is due to the transition of the smaller low spin Co^{III}ions to the larger high spin Co^{+3} or intermediate spin Co ^{III} ions with increasing temperature.

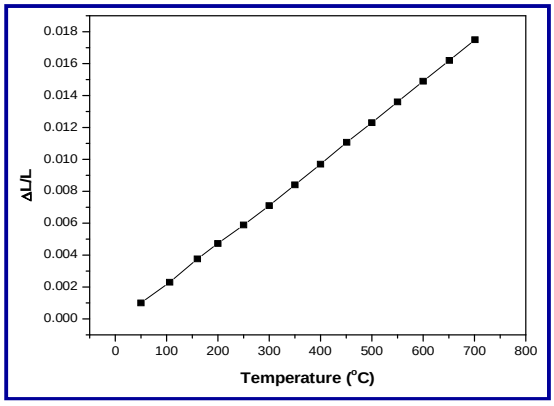

Fig. 5: Thermal expansion coefficient of $NdCoO_3$

4.7. Density Measurement Studies

Relatively dense samples with density greater than 96% of the theoretical value are required for the measurement of thermal expansion coefficient and electrical conductivity, the theoretical XRD density and the relative density (%) were measured and are given in **Table 1**. The low bulk density value of $NdCoO_3$ powder indicates the fine particle nature of the powder.

Table 1. Relative density of $NdCoO_3$

Sintering temp. (°C)	Bulk density(g/cc)	Theoretical density(g/cc)	Relative Density(%)
800	7.0323	7.3330	95.9

4.8 Apparent Porosity Measurement

The apparent porosity values were obtained on $NdCoO_3$ sample for various sintering temperatureas shown in **Table 2.** The porosity decreased linearly

with increasing temperatures. The apparent porosity was observed to be 30.08 % at 800 °C and 18.19 % at 850 °C. The $NdCoO_3$ sample showed 30.08 % of apparent porosity after sintering at 800 °C for 5 h which is close to the desired porosity of the cathode material for IT-SOFC application.

Table 2. Variation of apparent porosity of $NdCoO_3$ at various annealing temperatures

Annealing temperature (°C)	Apparent porosity (%)
550	65.09
650	53.02
750	43.00
800	30.08
850	18.19

4.9 Electrical conductivity

Generally, there are two kinds of conductive mechanisms namely, electronic and ionic conductivity in $NdCoO_3$ type perovskite oxides, owing to the presence of holes and oxygen vacancies. While, the ionic conductivity is much lower than the electronic conductivity. Therefore, it can be assumed reasonably that the measured values refer to the electronic conductivity alone.

The logarithm of electrical conductivity (log σ) of the system as a function of the reciprocal temp. is shown in **Fig.6.** It indicates thatthemaximum electrical conductivity ofthe sintered sample is 460Scm^{-1}at 600°C for $NdCoO_3$nanocrystalline powder.

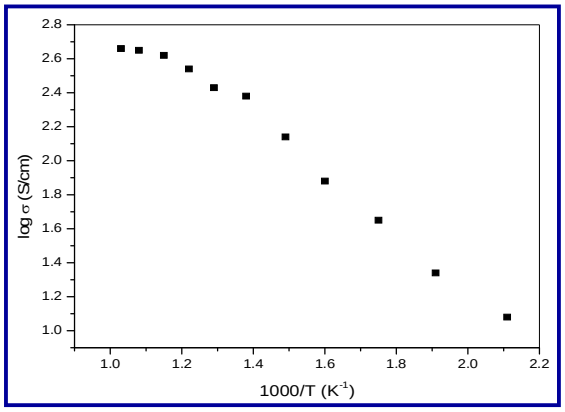

Fig. 6:Electrical conductivity of $NdCoO_3$

5. CONCLUSION

The nanocrystalline $NdCoO_3$ powder has been prepared successfully by a novel microwave assisted combustion method. The cubic provs kite $NdCoO_3$ was calcined at short microwave irradiation time (50 min). This calcination time is relatively lower than conventional solid state reaction methods. The large specific surface area and nanoparticle size can be achieved by microwave assisted combustion method to that of other conventional methods. In addition, electrical conductivity measurement revealed that the maximum conductivity of 460 S cm^{-1} was obtained in air at 600 °C, which is higher than the reported values.

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