Microwave Synthesis of Nd$_{1-x}$Ca$_x$CoO$_3$ Nanopowders as Cathode Material for Intermediate Temperature Solid Oxide Fuel Cells

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Abstract

Nd$_{1-x}$Ca$_x$CoO$_3$ (x=0.1, 0.2, 0.3, 0.4 and 0.5) nanopowders were synthesized by a microwave assisted combustion method using Neodymium(III)nitrate, calcium (II)nitrate, cobalt(II)nitrate and aspartic acid(fuel) in a domestic microwave oven with an optimized irradiation time of 50 min. This process remarkably reduced the synthesis time to obtain Nd$_{1-x}$Ca$_x$CoO$_3$ very quickly. The crystalline structure of Nd$_{1-x}$Ca$_x$CoO$_3$ nanopowders was confirmed by X-ray diffraction. The average crystallite size was determined from X-ray line broadening analysis by using the Scherer equation. The particle size was determined by TEM analysis. The structural morphology of the synthesized product was observed by SEM studies. The electrical conductivity studies revealed that Nd$_{0.6}$Ca$_{0.4}$CoO$_3$ possessed the maximum electrical conductivity of around 445 Scm$^{-1}$ at 500°C which was determined from dc-four probe method.

Keywords: Nd$_{1-x}$Ca$_x$CoO$_3$; Microwave synthesis; IT-SOFC; Thermal expansion co-efficient; Electrical conductivity

I. INTRODUCTION

The solid oxide fuel cell (SOFC) is an electrochemical device that converts the chemical energy in to an electrical energy in a clean and efficient way. It has high energy efficiency and environmental advantage. A reduction in the operating temperature of SOFC can decrease materials degradation and facilitate the use of low cost metallic components such as interconnect instead of the more expensive ceramic interconnect which is particularly important for the planar design of SOFC. The electrodes are one of the main components in SOFC, and the use of alternative materials with improved performance is required for reduction in the opening temperature. The cathode material in 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.

Nanocrystalline powders can significantly enhance sintering rate, decrease sintering temperature and improve optical, electrical and magnetic properties compared to the micrometer size powders [1,2]. The state-of-the-art cathode material for high temperature (~1000°C) operation is La$_{1-x}$Sr$_x$MnO$_3$ perovskite oxide. However, its poor oxide-ion conductivity prevent its use for IT-SOFC [3,4]. La$_{1-x}$Sr$_x$CoO$_3$ has higher conductivity than La$_{1-x}$Sr$_x$MnO$_3$ but it is known to have problems of high Thermal expansion co-efficient (TEC) (22×10$^{-6}$°C$^{-1}$) which is much larger than gadolinium doped ceria electrolyte (CDO) [5]. Hence, the development of alternative cathode materials with adequate electrical conductivity with reduced TEC is needed to make the IT-SOFC technology successfully. Nd$_{1-x}$Sr$_x$CoO$_3$ exhibited the electrochemical performance with adequate electrical conductivity and larger TEC [6]. To lower the TEC, a newer Nd$_{1-x}$Ca$_x$CoO$_{3+δ}$ (0≤x≤0.5) cathode material by microwave-assisted combustion synthesis process using domestic microwave oven has been synthesized. In a microwave oven, heat is generated internally within the sample itself by the interaction of microwaves with the material [7] instead of originating from an external heating source as in conventional oven. Microwave synthesis is generally considered as a fast and very energy efficient. The
reaction occurs at lower temperatures in a much shorter time in microwave synthesis than in conventional combustion synthesis methods. [8] Microwave synthesis has products with good phase purity and degree of crystallinity [9,10] and nanoscale particles [11,12] with larger surface area [13] compared to conventional methods. Finally, the microwave assisted combustion derived products were characterized for their physical and electrical studies.

II. EXPERIMENTAL

The microwave assisted combustion synthesis process involves the dissolution of desired amount of Nd(NO₃)₃, Co(NO₃)₂, Ca(NO₃)₂, and aspartic acid (fuel) in small quantity of distilled water in order to form a homogeneous solution. The oxidizing valency (o) of Nd(NO₃)₃ is -15, Co(NO₃)₂ is -10 and Ca(NO₃)₂ is -10 and the reducing valency (F) of aspartic acid is +15. Hence the amount of aspartic acid required was calculated for NdₓCaₓCoO₃ system is (0.9x-15)+0.1x-10+(1x-10)+15n=0;x=1.6333M. Therefore, the required amount of aspartic acid was 1.6333M. The same procedure was followed for other ratios such as 0.2, 0.3, 0.4 and 0.5. The above homogenous solutions were taken in a glass beaker and kept in a microwave for 10 minutes irradiation to get a foam like metal-organic precursor. At this stage, the microwave oven was switched off and the foam-like powders were collected and then crushed. The crushed powder were taken in crucible and kept in a domestic microwave oven with a maximum output of 900W and a magnetron frequency of 2.45GHz. During microwave irradiation, aspartic acid on combustion released 900W and a magnetron frequency of 2.45GHz. During irradiation, aspartic acid on combustion released heat which also initiated the solid state reaction.

The microwave irradiation was performed at optimized time duration of 50 minutes to obtain phase pure NdₓCaₓCoO₃ nanopowders (Fig. 1).

A part of the calcined powder was used to take X-ray diffraction (XRD), scanning electron microscope (SEM) and the remaining part of the powder was mixed with 3% polyvinyl alcohol binder and pressed into pellets with a diameter of 13 mm under uniaxial pressure (200MPa). Dense samples were obtained by sintering the pellets at 1073K for 5 h in air with heating and cooling rate of 5°C/min. Rectangular bars of approximate dimensions of 7x3x1 mm³ were cut from the sintered pellets for the SEM, electrical conductivity and TEC measurements. The bars had a density in excess of 95% of the theoretical value was determined from the Archimedes method.

2.1 Characterization

The X-ray powder diffractometer (XRD) analysis (Model: Philips XPert MPD®) was used to identify the phase purity and structural confirmation. The diffraction patterns were obtained at 25°C in the range of 20° ≤ 2θ ≤ 80°. The structural morphology of the samples was observed using a JEOL Scanning electron microscopy (Model: JSM 840A). The calcined fine powders were examined by transmission electron microscope (TEM); JEOL (Model: 1200EX). The BET surface area was analysed by QuantaChrom Autosorb-1 surface area analyzer.

Thermal expansion coefficient (TEC) data were obtained using as dilatometer (SETSYS-1750, SETARAM) in the temperature range of 50 - 700°C with a heating rate of 10°C/min under an ordinary atmosphere [7]. The electrical conductivity of the sintered pellets were measured by a dc-four probe method using Keithley 2400 at various temperatures in the range of 200-700°C in air [7].

III. RESULTS AND DISCUSSION

3.1 X-ray diffraction studies

The X-ray diffraction pattern of NdₓCaₓCoO₃ (0≤x≤0.5) samples irradiated for 50 min in a microwave oven are shown in Fig. 2. Sample irradiated for 50 min had a single phase NdₓCaₓCoO₃ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5), without any noticeable impurity phase. All the XRD patterns were well indexed as a orthorhombic perovskite structure. These results strongly suggest that microwave assisted combustion method requires much lower calcination energy with shorter time duration than solid state reaction method, where the calcination temperature is usually 800-1000°C for more than 6h.

The average crystalline size was calculated using Scherrer formula [19]. The lattice parameters and lattice volume, and the average crystallite size of the samples are summarized in Table 1. The data indicate that the lattice parameters and lattice volume increased with Ca content (x) at A site of NdCoO₃ as shown in Fig. 3 & 4. The substitution of Nd³⁺ ions by larger Ca²⁺ ions (r=0.1340), caused oxidation of Co³⁺ ions (r=0.545A°) to smaller Co²⁺ ions (r=0.530A°) and the formation of oxide-ion vacancies.

3.2 Particle size analysis

From the XRD data of the as prepared powders NdₓCaₓCoO₃ (x=0,0.1,0.2,0.3,0.4,0.5 ) , the average particle size was calculated from X-ray line broadening analysis using Scherrer equation [14];

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]

where D is the average particle size, λ is the wavelength of Cu-Kα radiation, β 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 the NdₓCaₓCoO₃ nanopowders at various compositions are given in Table 1. The particle size measured from TEM and XRD. The smaller average crystallite size (nanoparticles) was achieved by using microwave assisted combustion method compared to conventional solid state reaction method [6]. But larger size of particles can be obtained for sintering pellets due to the nucleation of smaller particles at high temperature (873K).
Table 1 Crystal structure, lattice parameters and BET surface area of Nd$_{1-x}$Ca$_x$CoO$_3$

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c(Å)</th>
<th>Lattice Volume (Å$^3$)</th>
<th>Structure</th>
<th>Average crystalline size (Å)</th>
<th>BET surface area (m$^2$/g)</th>
</tr>
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<tr>
<td>0.0</td>
<td>5.3360</td>
<td>5.3509</td>
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<tr>
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<tr>
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<td>24.90</td>
<td>24.90</td>
</tr>
</tbody>
</table>

Synthesis of Nd$_{1-x}$Ca$_x$CoO$_3$ powder

Figure 1. Flow chart of microwave assisted combustion synthesis of Nd$_{1-x}$Ca$_x$CoO$_3$
3.3 SEM analysis

The scanning electron micrographs of as-prepared Nd$_{0.4}$Ca$_{0.6}$CoO$_3$ powder at 50 min. microwave irradiation time and sintered at 873K for 5h are shown in Fig.5. The prepared powders were highly porous and particles were linked together in agglomerates of different shapes and sizes. Substantial particle growth was observed upon sintering for 5h at 873K. But the structure remained highly porous, which resembled the typical cathode structure for SOFC.
Figure 4 Lattice volume of Nd$_{1-x}$Ca$_x$CoO$_3$

Figure 5 SEM photograph of Nd$_{0.5}$Ca$_{0.5}$CoO$_3$ (a) Calcined powder, b) Sintering pellet, c) Cross section of sintering pellet

3.4 TEM analysis
Fig. 6 shows TEM photographs of Nd$_{1-x}$Ca$_x$CoO$_3$ (x=0, 0.4) powders calcined at 50 minutes. Samples had fine nanocrystalline size particles (Table 1). The TEM results were agreed with XRD identification.

3.5 BET surface area analysis
The surface area of Nd$_{1-x}$Ca$_x$CoO$_3$ nanopowders was calculated and summarized in Table 1, which is higher than the same materials synthesized by other conventional methods [15]. The BET surface area did not vary with x in Nd$_{1-x}$Ca$_x$CoO$_3$.$\delta$.

3.6 Thermal expansion
The linear thermal expansion coefficient of Nd$_{1-x}$Ca$_x$CoO$_3$.$\delta$ (x=0, 0.1, 0.2, 0.3, 0.4, and 0.5) was obtained on heating from 50-700°C in air (Fig. 7). The average thermal expansion values calculated from its slope of the curve is shown as Fig. 8. The thermal expansion coefficient increased almost linearly with increasing temperature from 50-700°C. In the high temperature region for most compositions due to loss of oxide ion from the lattice, and TEC decreased with increase in x, due to the cell volume increased with Ca, and reached a minimum value of 14.00X10$^{-6}$ C$^{-1}$ at x = 0.3 and then increased with x ≤ 0.4 which is lower than Sr doped NdCoO$_3$ [6].

3.4 Electrical conductivity
The temperature dependence of electrical conductivity of Nd$_{1-x}$Ca$_x$CoO$_3$.$\delta$ is shown in Fig. 9. It shows the variation of electrical conductivity with Ca content (x) at various temperatures. At a given temperature, the conductivity value increased with x due to increasing Co$^{4+}$ content and the charge carrier concentration. The conductivity increased with temperature for x≤0.3, implying small polaron semiconductor behaviour, but decreased with increasing temperature for x > 0.3, implying the metallic behaviour. Thus Nd$_{1-x}$Ca$_x$CoO$_3$.$\delta$ exhibits, a semiconductor- to- metal transition around x =0.3.
The faster decrease in conductivity at higher temperatures for samples with \( x \geq 0.3 \) is due to the loss of oxygen from the lattice as shown in Fig. 6, and the cell volume increased with Ca content (x), it caused a decrease in TEC with x. \( \text{Nd}_{0.6}\text{Ca}_{0.4}\text{CoO}_3 \) possessed the utmost electrical conductivity of around 445 Scm\(^{-1}\) at 500ºC. These conductivity value is much higher than the reported value of \( \text{Nd}_{0.6}\text{Sr}_{0.4}\text{CoO}_3 \)\[6, 16, 17\].

**Figure 6** TEM photograph of \( \text{Nd}_{1-x}\text{Ca}_x\text{CoO}_3 \)(x=0, 0.4)

![Figure 6](image1.png)

(a)

![Figure 6](image2.png)

(b)

**Figure 7** Thermal expansion coefficient \( \text{Nd}_{1-x}\text{Ca}_x\text{CoO}_3 \)(0≤x≤0.5)

![Figure 7](image3.png)

**Figure 8** Average thermal expansion coefficient of \( \text{Nd}_{1-x}\text{Ca}_x\text{CoO}_3 \)(0≤x≤0.5)

![Figure 8](image4.png)
**Figure 9** Electrical conductivity of \( \text{Nd}_{1-x}\text{Ca}_x\text{CoO}_3 (0 \leq x \leq 0.5) \)

IV. CONCLUSION

\( \text{Nd}_{1-x}\text{Ca}_x\text{CoO}_3 (0 \leq x \leq 0.5) \) perovskite oxides had been synthesized successfully by microwave assisted combustion method using aspartic acid as a combustion fuel with in 50 min consuming shorter time and lower energy when compared with conventional methods. The synthesized nanoparticles had nanoparticles with high specific surface area. Its specific surface area and nanoparticle size did not vary significantly with x in \( \text{Nd}_{1-x}\text{Ca}_x\text{CoO}_3 \). In addition, electrical conductivity measurement revealed that \( \text{Nd}_{0.6}\text{Ca}_{0.4}\text{CoO}_3 \) possessed the maximum conductivity of 445 Scm\(^{-1}\) at 500°C in air, which was higher than the reported value of Sr doped \( \text{NdCoO}_3 \).

REFERENCES