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Preparation and Characterization of $NdCrO_3$ Cathode for Intermediate Temperature Fuel Cell Application

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Abstract

This work was focused on the synthesis of nano-crystalline powder by the assisted combustion method which was taken by metal nitrates and aspartic acid as fuel. The synthesized powder is characterized by particle size in X-ray diffraction (XRD) and metal complex formation in Fourier transform Infra-red Spectroscopy (FT-IR). The surface morphology of the crystalline powder was found out by Scanning electron microscope (SEM), and analytical technique used to determine the thermal stability in TGA& DTA. The electrical conductivity studies revealed that $NdCrO_3$ possessed the maximum conductivity determined from dc-four probe method.

Keywords: Fuel Cells, Electrical Conductivity, Cathode Material.

I. INTRODUCTION

Solid Oxide Fuel Cells (SOFCs) offers a clean, pollution free technology for the electrochemical generation of electricity at high efficiencies. A major obstacle for commercial applications of both materials and processing. Thus intermediate temperature Solid Oxide Fuel Cells (ITSOFCs), which can significantly reduce the costs of SOFC is also being studied.

The reduction of SOFC operating temperature brings critical problems such as low kinetics of the oxygen reduction reaction, it leads to large over potential at the electrode-electrolyte interface. Therefore, developing new cathode materials with good performance at low operating temperature is a key area of research for SOFC applications. The performance can be improved by a better control of the morphology of the different components and the reduction of the working temperature from 1000^0C to below 800^0C is likely to preserve the stability besides allowing the use of metallic interconnects instead of ceramic-based ones.

The high operating temperature of SOFC increases the electrode reaction rates but also enhances degradation of components and thus decreases the cell durability. A desirable cathode material for intermediate temperature SOFCs should have high electronic and oxide ion conductivities, low thermal expansion to be compatible with the electrolyte, as well as high catalytic activity for the oxygen reduction reaction.

The studies of the rare earth transition metal oxides have revealed many fascinating aspects. Among all the rare earth orthoferrites, the $NdCrO_3$ is an orthorhombically distorted perovskite. $NdCrO_3$ has attracted a great deal of researches in various fields including photonics, advanced materials surface catalytic systems and protective coatings. $NdCrO_3$ has gained considerable attentions in various applications.

The incorporation of neodymium (Nd) ions in insulating layers has important applications for solid state laser materials, luminescent materials, protective coatings and gate dielectric applications.

Based on reported literatures and on our preliminary feasibility studies in the present work, $NdCrO_3$ nanoparticle has been synthesized through inorganic complex intermediate using green ligation agents obtained from natural waste resources. $NdCrO_3$ synthesis via neodymium-ellagate complex has been described and studied at room temperature. This is particularly advantageous because this method utilizes natural ligation agent.

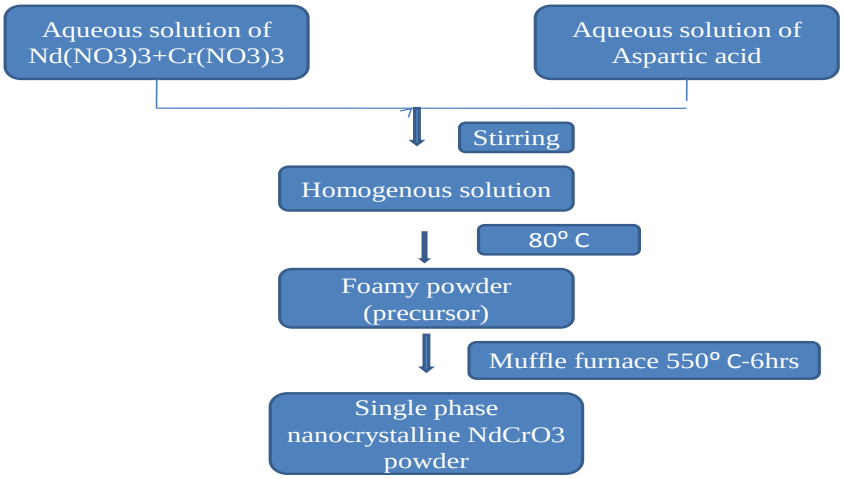
II. EXPERIMENTAL STUDIES

2.1 Materials Used

We used Neodymium nitrate $Nd(NO_3)_3$ (99.9%), Chromium nitrate $Cr(NO_3)_3$ (99.99%) and Aspartic acid ($C_4H_7NO_4$) were purchased from Sigma-Aldrich. All of the Chemicals were used without further purification.

2.2 Preparation

The $NdCrO_3$ was synthesized by assisted combustion method which using $Nd(No_3)_3$, $Cr(No_3)_3$, and Aspartic acid ($C_4H_7NO_4$) were (purity>99.9%, Aldrich) used. All the substances, required stoichiometric ratio were dissolved in double distilled deionised water. The Aspartic acid was used as fuel. All of the solutions were mixed together to form homogeneous solution This solution becomes dark blue in colour and it was kept at constant heating at 80^{o} C.



To obtain foamy –like powder, it was continuously heated and crushed. The crushed powder was taken in a crucible and heated in muffle furnace at 550°C for 6 hrs.

III. **CHARACTERIZATION:**

IR Spectra were recorded on perkin-Elmer in range 4000-400 cm^{-1} using Agilent Cary 630 FTIR Spectrometer instrument. Samples were kept directly without KBr pellets.

Thermal analysis was carried out in a meter TA3000 system equipped with a TC10 processor unit. Thermogravimetric curves were obtained in a TG50 unit, which working at a heating rate of 10^{o} C min^{-1}. The measurements were performed upon cooling in the temperature range from 800 to 100^{0} C at a cooling rate of 5^{0} C/min.

X-ray diffraction analysis was carried out on powders in different molar relations oxidant-fuel (nitrate salts-aspartic acid) for crystalline phase identification. Powder XRD patterns were recorded at room temperature using a step scan procedure in the 2θ range 20-80^{0} on a JEOL JSM-840 diffractometer equipped with a crystal monochromator employing Cu-Kα radiation.

Scanning Electron Miroscopy(SEM) was used at different magnifications to observe the surface morphology of the samples.

The Particle size of the nanoparticle powder was determined by Transmission Electron Microscopy (TEM.)

The four probe used to determine the electrical conductivity of $NdCrO_3$ sintered pellet, which is heated in the temperature range 200 -700^{0}C in air. All the samples show a decrease in electrical conductivity with increasing temperature, showing the metallic behavior over the entire temperature range.

IV. RESULTS AND DISCUSSION

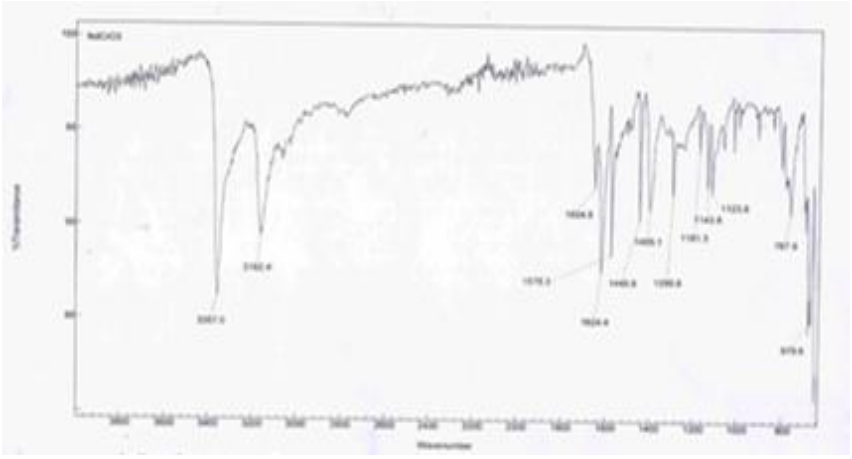


Figure 4.1: FTIR Spectrum of $NdCrO_3$

The IR Spectrum of CrO_2 showed the principle peaks at 3357.0cm^{-1} ,3162.4cm^{-1} and 1578.3cm^{-1} are due to the bending and stretching vibration of hydroxyl group(-OH). FTIR Spectra showed strong bond at 679.6cm^{-1}which due to stretching vibration of the Nd-O bond in the structure.

The peak appeared at 1449.8cm^{-1} and 1405.1cm^{-1} corresponds to the H-OH bond mode confirming the presence of moisture in the sample.

The bond appeared at 1299.8cm^{-1} is due to the presence of CO_2 in the sample. The Sample $NdCrO_3$ exhibited peak at 767.9cm^{-1}. The vibration peaks at 1181.3cm^{-1},1143.8cm^{-1},1123.8cm^{-1} it corresponds to most of the peaks for cathode material as described in literature. The band at about1654.8cm^{-1}, and 1624.4cm^{-1},which is the result of the –C=O, via coordinating bonding.

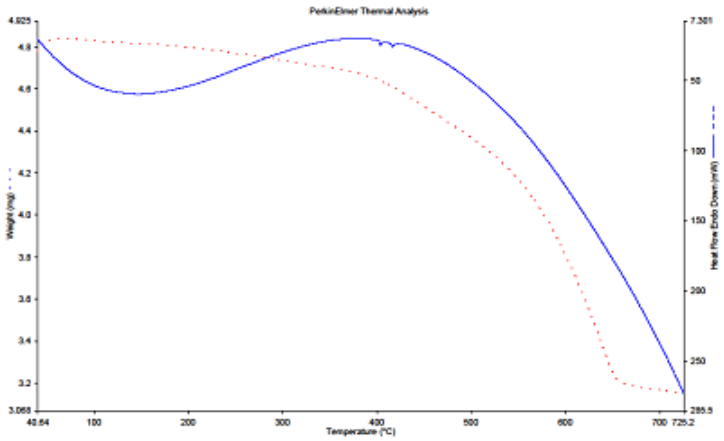


Figure 4.2: TGA & DTA analysis of $NdCrO_3$

The result of the thermogravimetric analysis of $NdCrO_3$ cathodes with temperature in air shown in this fig (4.2). These data collected by the weight change of $NdCrO_3$ samples. In TGA the first weight loss in between 300-520^0 C in the sample due to the removal of moisture in 4.0-4.6mg, it was observed above 520^0 C, and the weight loss continued beyond 630^0 C.

The peak associated in DTA graph, the two broad exothermic peak at 150^{o}C occurred due to weight losses between 4.4-4.6mg, and the second peak is 410^{o}C weight losses between 4.6-4.8mg, and the weight losses continued upto 700^0 C.

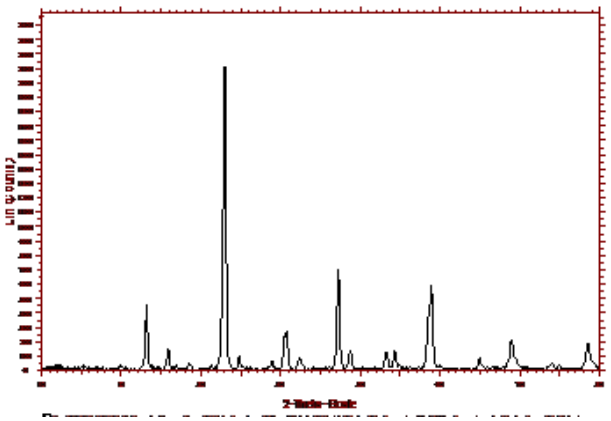


Figure 4.3: XRD Analysis of $NdCrO_3$

It can be seen that this sample is single phase orthorhombic perovskite structure at room temperature. The color of the pure $NdCrO_3$ compound was dark green. The unit cell lattice parameter with a least-square refinement from the XRD patterns, and the results are shown, a= 0.54766 nm is good in agreement with the studies reported by references 9and 10.

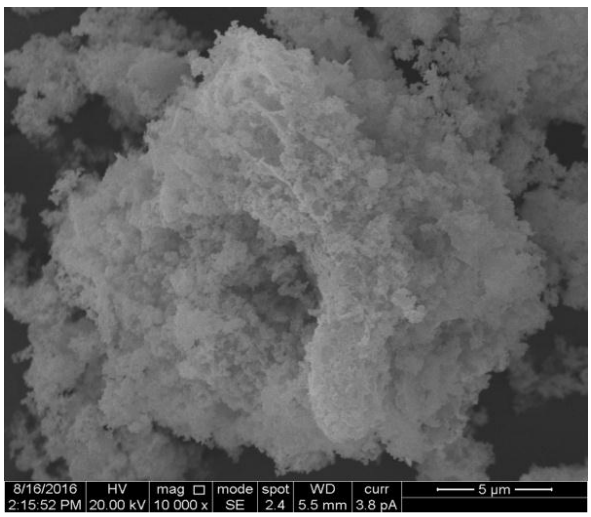


Figure 4.4: SEM Analysis of $NdCrO_3$

The electrode microstructure is related to the characteristics of the surface area, electrochemically active area, volume fraction of chemical phases present and electron transport. This sample shows porous morphology properties in the cathode as well as connectivity between the cathode. The microstructure of $NdCrO_3$ sample is similar to that the microstructure of the sample is insensitive to this substitution.

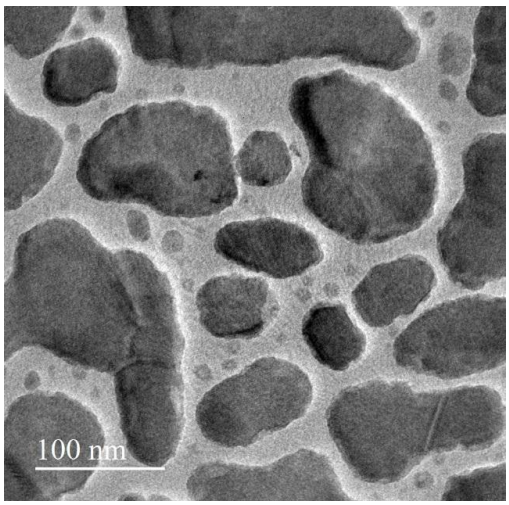


Figure 4.5: HRTEM micrograph of the $NdCrO_3$

The morphology of $NdCrO_3$ Nanoparticle is characterized by High resolution transmission electron microscopy. It can be observed from the HRTEM images that the particles are found to be spherical in shape and a small agglomeration was observed. This due to the high surface interaction between nanoparticles which have large specific area and high surface energy.

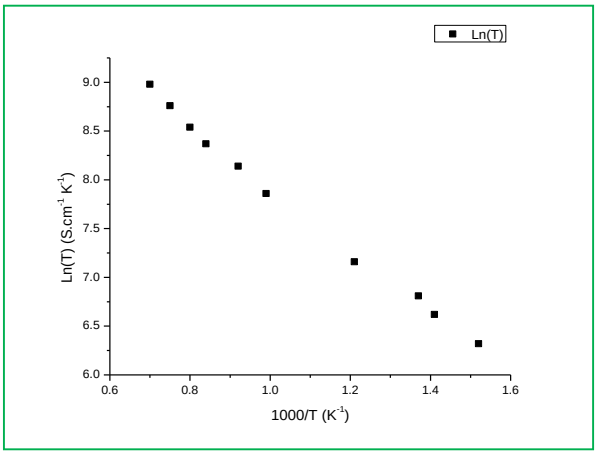


Figure 4.6: Electrical Conductivity of $NdCrO_3$

The electrical conductivity of $NdCrO_3$ was also measured in air and in hydrogen at different temperatures (Fig. 4.6). The electrical conductivity of $NdCrO_3$ shows a sharp decrease in H_2 as compared with that in air, which leads to the decrease of the electrical conductivity as the concentration of small polarons decreases. The electrical conductivity of $NdCrO_3$ is **1.1 S/cm** at 850^0 C in hydrogen, above the minimum electrical conductivity of **1 S/cm** for the interconnect application in SOFCs. Thus, the electrical conductivity of $NdCrO_3$ in a reducing environment is also adequate for the application as an interconnect material for SOFCs.

5. CONCLUSION

The combustion technique considerably reduces the sintering temperature and time also yields nanostructured $NdCrO_3$ solid solutions. The temperature- dependent conductivity exhibits a transition at 850^o C for $NdCrO_3$ within the solid solubility limit. The $NdCrO_3$ cathode is thermos chemically stable, though it reacts chemically with YSZ at high temperature. $NdCrO_3$ prepared using the combustion technique, promises to be a potential cathode for ITSOFC applications.

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