

## Preparation And Characterization Of $\text{Nd}_{1-x}\text{Ca}_x\text{CrO}_3$ Cathode Material For Intermediate Temperature Solid Oxide Fuel Cells

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**Abstract:** The crystal chemistry, thermal studies, electrical conductivity of  $\text{Nd}_{1-x}\text{Ca}_x\text{CrO}_3$  ( $0 \leq x \leq 0.5$ ) have investigated. The orthorhombic structure of crystalline sample and lattice constant increases with increasing Ca content(x). The conductivity increases with increasing  $\text{Ca}^{2+}$  Contents upto  $x=0.3$ . The electrical conductivity can be described by the small polaron hopping conductivity mechanism. Calcium doping significantly depresses the chromium vapourization of  $\text{NdCrO}_3$  Chemical compatibility and thermal stability under condition this cathode material can be considered as intermediate temperature solid oxide fuel cell.

**Keywords:** Fuel Cell, Electrical Conductivity,

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Date of Submission: 11-11-2017

Date of acceptance: 28-12-2017

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### I. Introduction

Research in the field of cathode material is very active, fostered by the current development of solid oxide fuel cells working at intermediate temperature. Solid Oxide Fuel Cell (SOFCs) are theoretically highly efficient and fuel-flexible systems. Current SOFCs operate at high operating temperature (800-1000 °C) its limit for cell and ancillary components, enhances cell performance degradation and elemental interdiffusion between components, and increases sealing difficulties. In particular, the rapid increase of cathodic polarization resistance with reducing temperature it contributes to the reduction in cell performance because oxygen reduction kinetics.

Many efforts have been developed to devote the performance, cathode material for intermediate temperature SOFCs. These perovskite and perovskite based- oxides such as  $\text{Nd}_{1-x}\text{Ca}_x\text{CrO}_3$  it exhibit a good electro-catalytic activity for the oxidation of hydrogen. In this current work, these samples were used as starting materials for a detailed study of the evolution of catalyst nanostructure as induced. These catalyst compositions were investigated which using high-resolution transmission electron microscopy (HR TEM), X-ray Diffractometer (XRD), Scanning electron microscopy (SEM), Electrical conductivity. In this present study is an assessment of the electrical parameters of Calcium doped neodymium Chromate at different temperature, from 700 - 900°C, and evaluation of its behavior as a component of symmetric SOFC.

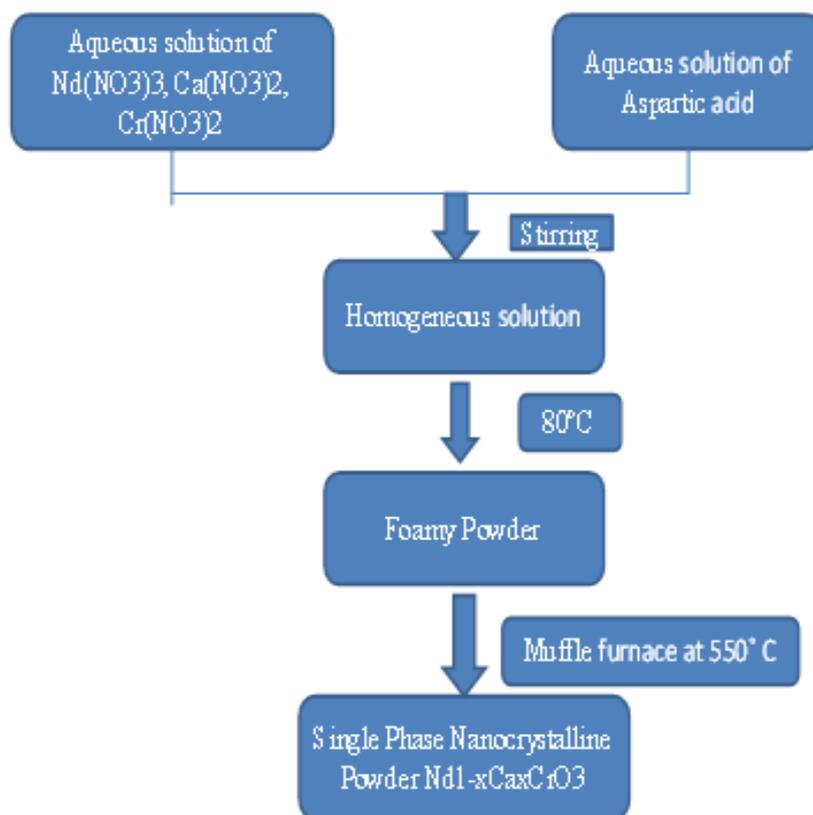
### II. Experimental

#### 2.1 Materials Used

We used Neodymium nitrate  $\text{Nd}(\text{NO}_3)_3$  (99.9%), Calcium nitrate  $\text{Ca}(\text{NO}_3)_2$  (99.99%) and Chromium nitrate  $\text{Cr}(\text{NO}_3)_2$  (99.9%) and Aspartic acid ( $\text{C}_4\text{H}_7\text{NO}_4$ ) were purchased from Sigma-Aldrich. All of the Chemicals were used without further purification.

#### 2.2 Preparation

The  $\text{Nd}_{1-x}\text{Ca}_x\text{CrO}_3$  was synthesized by assisted combustion method which using  $\text{Nd}(\text{NO}_3)_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_2$  and aspartic acid ( $\text{C}_4\text{H}_7\text{NO}_4$ ) were (purity > 99.9%, Aldrich) used. All the substances, required stoichiometric ratio, were dissolved in double distilled de ionized water. The Aspartic acid was used as fuel. All of the solutions were mixed together to form homogeneous solution. This solution becomes dark green colour and it is kept at constant heating at 80°C. To obtain foamy-like powder it was continuously heated and then crushed. The crushed powder was taken in a crucible, and heated on muffle furnace at 550°C for 6 hrs. The same procedure was followed by other ratio such as 0.3, 0.5.



The structural study and the determination of the lattice parameters of the oxides were performed at room temperature by X-ray powder diffraction (XRD) on a Siemens diffractometer using CuK<sub>α</sub> radiation. The XRD data were collected by step scanning in the  $10 \leq 2\theta \leq 20$  in increments of  $0.02^\circ$ . The lattice parameters were determined using a least Squares unit cell refinement computer program. The thermal expansion of the samples was measured in air using a dilatometer. The measurements were performed upon cooling in the temperature range from 800-100°C at a cooling rate of 5°C/min. Microstructural Characterization of the cathodes and the interfacial reaction analysis were carried out in scanning electron microscope (SEM). Samples for transmission electron microscopy (TEM) were prepared from powders suspended and ultrasonically dispersed in butanol. One drop of the suspension was placed on a Cu grid with holey carbon film. Selected area electron diffraction (SAED) and high resolution TEM (HRTEM) experiments were performed using a JEOL 3000F microscope with a resolution limit of  $\approx 1.1 \text{ \AA}$ , which is equipped with an X-ray energy dispersive spectroscopy (XEDS) microanalysis system (OXFORDINCA). HRTEM images were recorded with an objective aperture of 70μm centered on a sample spot within the diffraction pattern area. Fast Fourier Transforms (FFT) of the HRTEM images were carried out to reveal the periodic contents of the HRTEM images using the Digital Micrograph package. The experimental HRTEM images were compared to simulated images using MacTempas software. Such computations were performed using information from (a) the structural parameters obtained from Rietveld refinement, (b) the microscope parameters of operating voltage (300 kV) and spherical aberration coefficient (0.6 mm), and (c) the specimen parameters of zone axis and thickness. The defocus (f) and sample thickness FTIR Spectra were recorded on FTIR Spectrometer (Agilent Cary 630 FTIR Spectrometer) using. The electrical Conductivity of the sample was measured by a standard four-probe technique in the temperature range of 300°C-850°C in air.

### III. Results And Discussion

#### 3.1 XRD Analysis

In XRD Patterns of Nd<sub>1-x</sub>Ca<sub>x</sub>CrO<sub>3</sub> ( $0 \leq x \leq 0.25$ ) Samples at 550°C for 6 h. XRD Analysis of the powders obtained after combustion, shows the perovskite formation. In all the samples are single phase with an orthorhombic perovskite structure at room temperature. All the diffraction peaks were found, it indicating that the Ca<sup>2+</sup> ion doping.

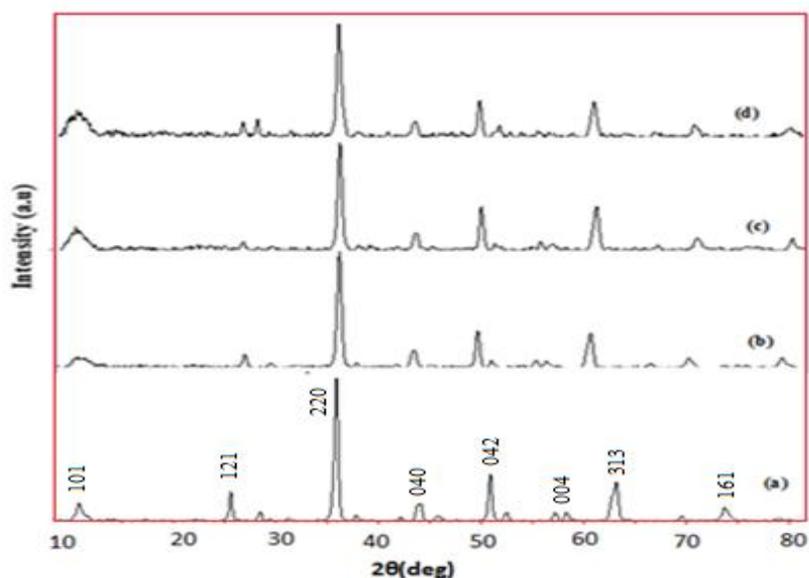


Fig 4.1 XRD Image of  $Nd_{1-x}Ca_xCrO_3$

#### 4.2. SEM Analysis

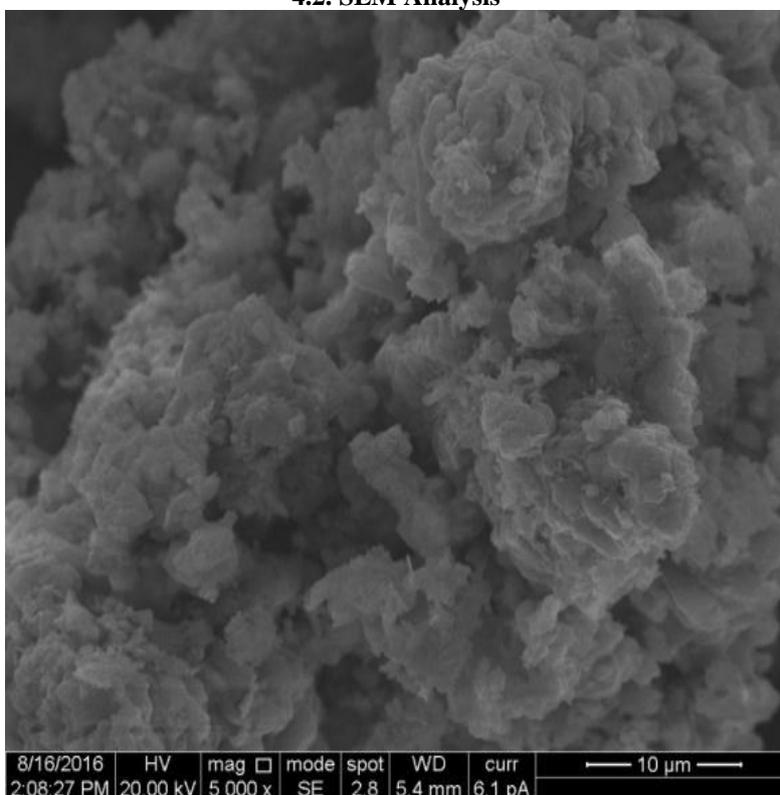
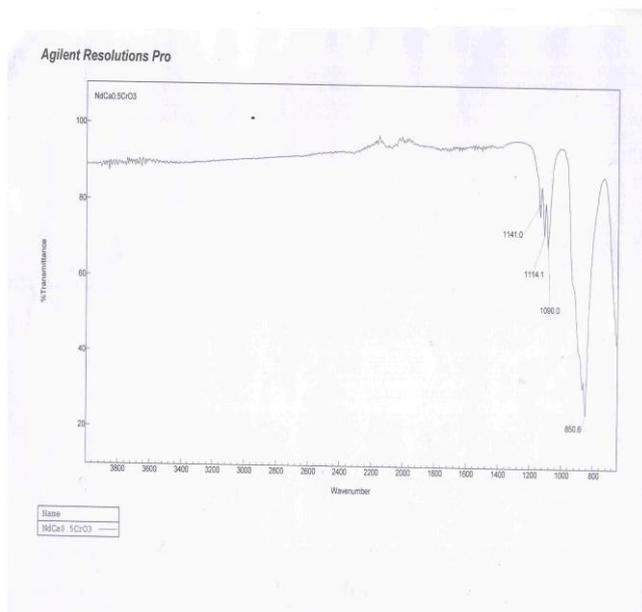


Fig 4.2 SEM Image of  $Nd_{0.9}Ca_{0.1}CrO_3$

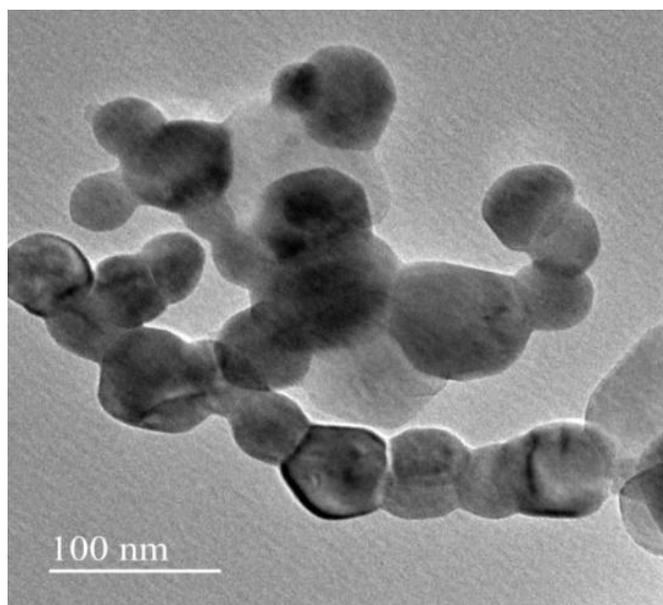
In aim to check the influence of these structural changes due to partial substitution of the cations on their morphology. SEM images of the perovskite of this series were recorded. As it can be seen, the sizes of the particles over range 3-10μm with a larger and wider distribution for pure  $NdCrO_3$  powders. Fig 4.2 shows the SEM Micrographs of the  $Nd_{1-x}Ca_xCrO_3$  Powders after Calcination at 550°C for 6 h. As it can be seen, the sizes of the particles are over a range of 1-10μm. It can be seen that pure  $NdCrO_3$  consists of symmetrical. However, the porosity in the sample is distinctly visible. With the calcium doping in  $NdCrO_3$  oxides, the geometrical shape of the  $Nd_{1-x}Ca_xCrO_3$  grain changes, and the porosity in the samples decreases significantly. A highly dense microstructure with almost no porosity has been obtained for the sample  $Nd_{1-x}Ca_xCrO_3$ .

### 3.FTIR Studies



**Fig 4.3** FTIR Spectrum of  $Nd_{0.5}Ca_{0.5}CrO_3$

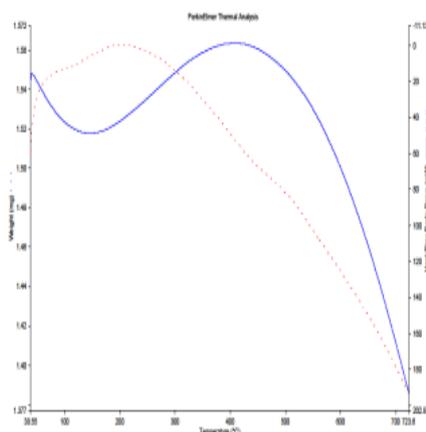
The strong bands observed in between 800-900  $cm^{-1}$  in the sample indicates the presence of metal oxygen bonds in their structure. It is accounted for the asymmetrical structure. A strong peak appeared at 850.6  $cm^{-1}$  and 872.9  $cm^{-1}$  in complexes. A few weak intensity bands in the range of 1114.1, 1089.7, 1119.0  $cm^{-1}$ .



**Fig.4.4.**HRTEM Micrograph of  $Nd_{0.7}Ca_{0.3}CrO_3$

Fig 4.4 Shows the TEM images of  $Nd_{0.7}Ca_{0.3}CrO_3$  Nanocrystalline powder. This image of a group of nanostructure scattering on the copper mesh. It is clear that the central part of the nanostructure is bright in contrast to its edge, it illustrating the hollow-insides of the particles were characterized. However, the breath of the particles of only about one or several micrometers, much shorter than that observed in SEM images. This phenomenon arises from the strong ultrasonic vibrations prior to the sample preparation for TEM analysis.

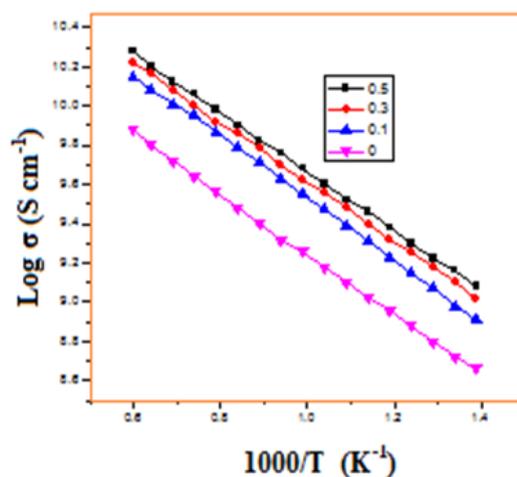
#### 4.5. TGA& DTA Analysis



**Fig 4.5** TGA&DTA Analysis of  $Nd_{0.9}Ca_{0.1}CrO_3$

In TGA curve the first weight loss is 100-200°C. The major weight loss occurs in between 300-450°C. The observed weight loss is 2-3% beyond 450°C is very minimal suggesting the formation of very little amount of amorphous chromate. Almost no weight loss above 250°C in samples prepared at reflux and at higher temperature suggested the formation of highly crystalline  $CrO_3$  in as-synthesized materials. In DTA curve one endothermic peak and two slight exothermic peaks are observed at 100-150, 260°C. The endothermic peak appear at 266.35°C indicated that decomposition or oxidation reactions occurred strongly at this temperature. The other exothermic peaks are attributed to the pyrolysis of nitrates on the precursor. These conclusion based on DTA analysis that the content of carbon and hydrogen in the precursor were decomposed completely below 300°C.

#### 4.6. Electrical Conductivity



**Fig4.6.** Electrical Conductivity of  $Nd_{1-x}Ca_xCrO_3$

Fig 4.6 Shows the dependence of electrical conductivity with temperature under the different atmospheres here tested. As observed the conductivity increases slightly for the doped compositions, especially for those with smaller amount of Ca. The formation accomplished by charge compensation for divalent cations such as  $Ca^{2+}$ . The ionic conductivity is increased at higher temperatures and high  $Ca^{2+}$  substitution. The electrical conductivity of this  $Nd_{1-x}Ca_xCrO_3$  was also measured in air and in hydrogen at different temperatures. The electrical conductivity of  $Nd_{1-x}Ca_xCrO_3$  is 1.1 S/cm at 850°C in hydrogen, above the minimum electrical conductivity of 1 S/cm for the interconnect application in SOFCs.

#### IV. Conclusion

Nd<sub>1-x</sub>Ca<sub>x</sub>CrO<sub>3</sub> have been synthesized, characterized, and evaluated as cathode materials for IT-SOFCs. The XRD and TEM results showed that the synthesized powder possessed the expected crystal structure, was single- phase had good crystallinity. These two methods have excellent agreement, giving the value for powder calcined at 1600 °C for 1hr, particle size was seen to occupy a narrow size range. The electrical conductivity of pellets sintered from the powder was measured structure, and cathode performance of NCC<sub>x</sub> indicates the performance for these materials are surface composition dependent crystallographic parameters.

#### References

- [1]. T. Jardiel<sup>a</sup>, M.T. Caldes<sup>a,\*</sup>, F. Moser<sup>a</sup>, J. Hamon<sup>a</sup>, G. Gauthier<sup>b,c</sup>, O. Joubert<sup>a</sup> New SOFC electrode materials: The Ni-substituted LSCM-based Compounds (La<sub>0.75</sub>Sr<sub>0.25</sub>)(Cr<sub>0.5</sub>Mn<sub>0.5-x</sub>Ni<sub>x</sub>)O<sub>3-δ</sub> and (La<sub>0.75</sub>Sr<sub>0.25</sub>)(Cr<sub>0.5</sub>Ni<sub>x</sub>Mn<sub>0.5-x</sub>)O<sub>3-δ</sub> Journal of Solid State Ionics 181(2010) 894-901.
- [2]. D. Beckel<sup>†</sup>, A. Bieberle-Hutter, A. Harvey, A. Infortuna, U.P. Muecke, M. Prestat, J.L.M. Rupp, L.J. Gauckler, Thin films for micro solid oxide fuel cells, Journal of Power Sources, 173(2007)325-345.
- [3]. Jie-Wei Yin<sup>\*</sup>, Yi-Mei Yin<sup>†\*</sup>, Jun Lu<sup>\*</sup>, Chunming Zhang<sup>\*</sup>, Nguyen Q. Minh<sup>‡</sup>, and Cells, The Journal of Physical Chemistry 2014,118,13357-13368.
- [4]. Xinge Zhang<sup>\*</sup>, Mark Robertson, Sing Yick, Cyrille Deces-petit, Edward Styles, Wei Qu, Yongsong Xie, Rob Hui, Justin Roller, Olivera Kesler, Radenka Maric, Dave Ghosh, Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub>+ Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> Composite Cathode for Cermet Supported thin Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> electrolyte SOFC Operating below 600 °C, Journal of Power Sources,160(2006)1211-1216.
- [5]. Marcin R. Kosinski, Richard T. Baker<sup>\*</sup>, Preparation and Property –Performance relationships in samarium-doped Ceria Nanopowders for Solid oxide fuel cell electrolyte, Journal of Power Sources, 196(2011)2498-2512.
- [6]. R.T. Baker<sup>\*,†</sup>, L.M. Gomez-Sainero<sup>\*\*</sup>, and I.S. Metcalfe<sup>\*\*</sup>, Pretreatment –Induced Nanostructural Evolution in CeO<sub>2-x</sub>, Sm<sub>2</sub>O<sub>3-x</sub> and CeO<sub>2</sub>/ Sm<sub>2</sub>O<sub>3</sub> supported Pd Catalyst for Intermediate-Temperature Methanol Fuel cells, Journal of Physical Chemistry 2009,113, 12465-12475.
- [7]. G. Ch. Kostogloudis<sup>\*</sup> and Ch. FtiKos Characterization of Nd<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3±δ</sub> SOFC Cathode Materials, Journal of the European Society 19 (1999) 497.
- [8]. Yu Shen, Monan Liu, and Tianmin He<sup>\*</sup>, San Ping Jing, Preparation, Electrical Conductivity, and Thermal Expansion Behaviour of dense Nd<sub>1-x</sub>Ca<sub>x</sub>CrO<sub>3</sub> Solid Solutions, Journal of American Ceramic Society 92 (10) 2259-2264 (2009).

IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

M.Nithya."Preparation And Characterization Of Nd<sub>1-x</sub>Ca<sub>x</sub>CrO<sub>3</sub> Cathode Material For Intermediate Temperature Solid Oxide Fuel Cells." IOSR Journal of Applied Chemistry (IOSR-JAC) 10.12 (2017): 41-46.