

Synthesis and Characterization of Strontium Doped Lanthanum Cobaltite thin films for SOFC Cathode

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Abstract: Different types of ceramic materials are currently being studied as possible cathodes in solid oxide fuel cell (SOFC), due to reduce operating temperatures. Strontium doped lanthanum cobaltite ($La_{1-x}Sr_xCoO_{3-\delta}$ -LSC) was used as cathode for solid oxide fuel cell (SOFC). LSC thin films with 0.1, 0.2 and 0.3 mol % strontium were synthesized by spray pyrolysis technique. These thin films were sintered at 1000°C has been characterized by X-ray diffraction to determine the crystalline perovskite phase; FESEM was used for morphological analysis. D. C. electrical conductivity was measured with variation of temperature and it increases due to increase of strontium content. Dielectric constant was measured with frequency variation.

Keywords: Spray Pyrolysis, Electrical conductivity, Dielectric constant, Cathode, LSC, SOFC.

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I. Introduction

Recently, solid oxide fuel cell (SOFC) studies on cathode development have focused on lanthanum strontium cobaltite (LSC). Lanthanum strontium cobaltite has been investigated as they are widely applied to high temperature ionic devices such as SOFCs, oxygen monitors and gas-separation membranes for its high electronic conductivity [1]. Strontium doped lanthanum cobaltite show mixed ionic-electronic conduction and high catalytic activities for oxygen reduction. LSC is also used in a number of other applications such as gas sensors, oxygen catalyst.

Thus, many different methods have been utilized to synthesize LSC thin film, such as chemical vapour deposition (CVD), physical vapour deposition (PVD), and sol-gel, dip-coating, screen printing technique, electrostatic spray deposition, r-f magnetron sputtering, and spray pyrolysis [2-6]. Among these methods, the spray pyrolysis is simple, cost effective, producing uniform and controllable film thickness. For SOFCs application, homogenous, crack-free and high purity thin films are required. The LSC thin films were prepared by cost effective spray pyrolysis technique by optimizing the substrate temperature, spray rate, substrate to nozzle distance. The spray pyrolysis technique was employed in this work to synthesize LSC thin film with composition ($La_{1-x}Sr_xCoO_{3-\delta}$) and films were sintered at 1000°C for 2 hours. The crystal structure, morphology and electrical properties were studied.

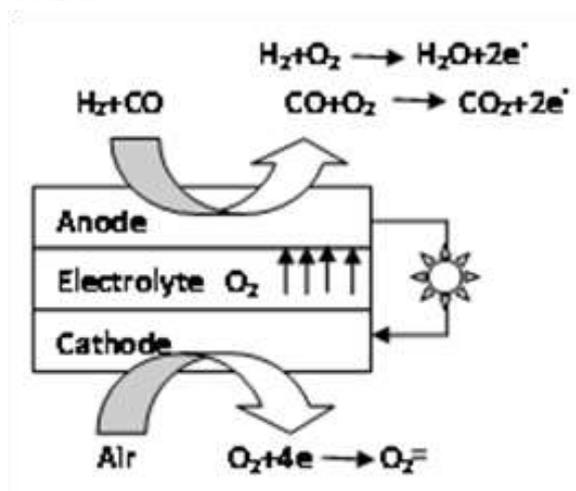


Fig. 1 Solid Oxide Fuel Cell

II. Experimental

The Lanthanum Strontium Cobaltite ($\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$) thin films were deposited on alumina substrate by using chemical spray pyrolysis technique. The basic principle used in chemical spray pyrolysis technique is that, a smallest droplet of the precursor solution sprayed from nozzle, reaches to the hot substrate leads to the pyrolytic decomposition of the solution which forms the adherent thin films in the presence of air as neutral gas [7].

The details of the preparation procedure of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC) thin film are given in the schematic diagram shown in fig.2. Lanthanum nitrate, strontium nitrate and cobalt nitrate were used as precursors of La, Sr and Co components. This precursor solution is used to deposit LSC thin films on alumina substrate at deposition temperature of 225 °C, this further leads to pyrolytic decomposition of these metallic salts and formation of lanthanum strontium cobaltite thin film [8]. The as deposited thin films were sintered at 1000°C in the muffle furnace for 2 hours. The crystal structures of the sintered LSC thin films were studied by X-ray diffraction (Bruker X-Ray Powder diffractometer) with Cu K α radiation ($\lambda= 1.5418\text{Å}$.U.) and the morphology was studied by field emission scanning electron microscope (FE-SEM). Dielectric constant was measured as a variation of frequency by LCR meter. D.C. conductivity measurement of LSC thin films were carried out by two probe resistivity setup.

III. Results and Discussion

3.1 Film formation:-

Fig.2 shows schematic flow-chart of spray pyrolysis technique. The deposition of thin films via spray pyrolysis involves spraying a metallic salt solution on a heated substrate. The solution droplets reach the substrate surface, where solvent evaporation and decomposition of the metal salt occurs, forming a film. Many processes occur sequentially and simultaneously during the formation of thin film by spray pyrolysis i.e. transport and evaporation of solution drops, solution spread on the substrate, evaporation of solvent. The drops of solution are transported and eventually evaporate. The substrate temperature and solution concentration are significant parameters which are responsible for the thickness and morphology of the thin films. A good morphology and uniform thin film was reported at 0.05M concentration. So solution concentration was varied from 0.01 M to 0.1 M keeping the substrate temperature fixed at 225 °C .

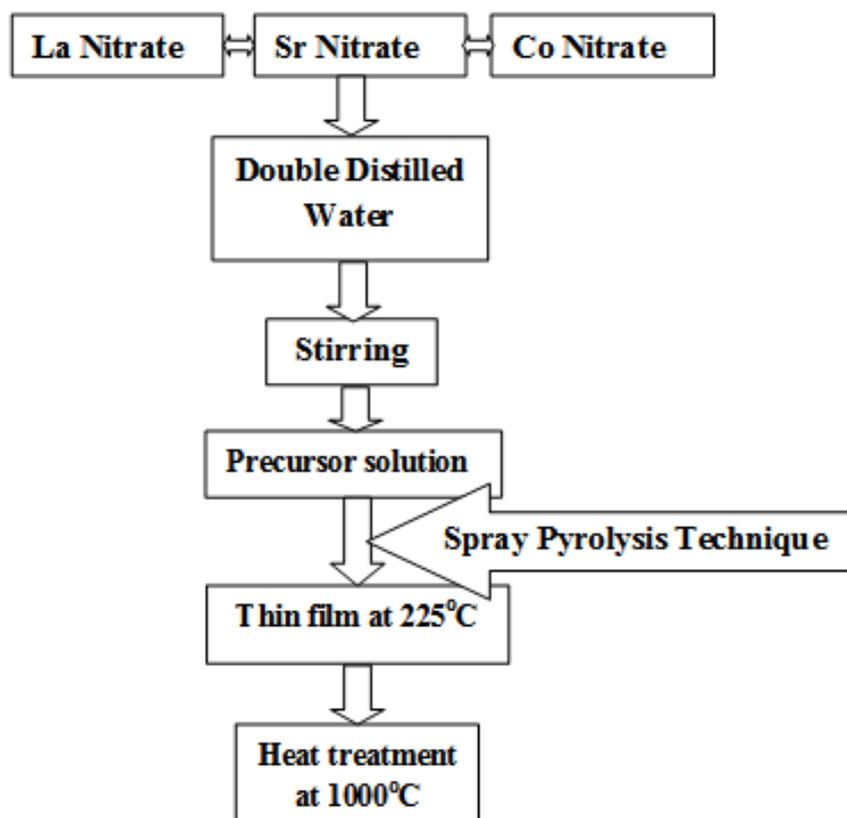


Fig. 2 Flow chart of spray deposition technique

3.2 XRD studies:-

XRD pattern of lanthanum strontium cobaltite thin films are shown in fig.3. The thin films clearly presented a well crystallized perovskite phase. XRD peaks were noticeably broadened. The planes observed are (104), (202), (214), (208), in XRD confirms crystallized rhombohedral structure with space group $R\bar{3}C$.

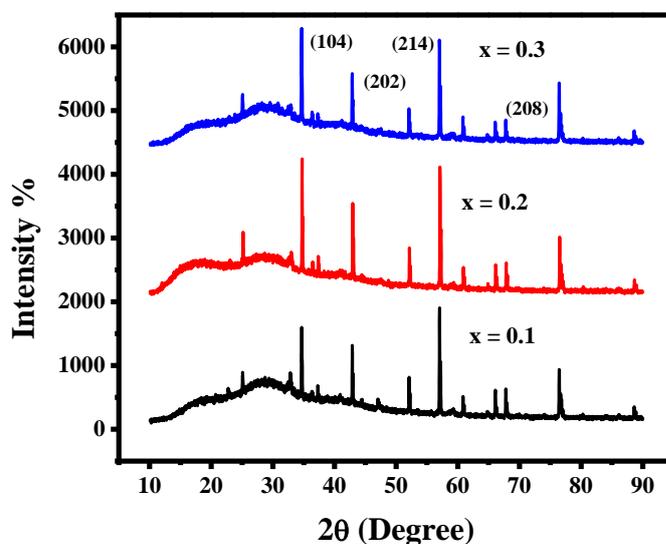


Fig. 3 The XRD of LSC sintered at 1000°C

3.3 Morphological Characterization:-

The surface morphology of LSC nanoparticles was studied by using FESEM. Fig.4 shows FE-SEM images of LSC sample sintered at 1000°C for 2 hours and compositions X = 0.1, 0.2 and 0.3 respectively. It was observed that the LSC thin film were well adhered to the substrate. All samples of LSC showed that they have fine and little tendency to formation of agglomerates exhibiting porosity^[9]. Such a porous structure is suitable for cathode of SOFC for oxygen to diffuse to the interface for the reduction to occur, which poses a high active surface area. As can be seen here the particles have spherical shape and also strontium content increases particles became more porous. The particle size of the sample reduced obviously due to the decrease of unit cell volume with the strontium content increasing.

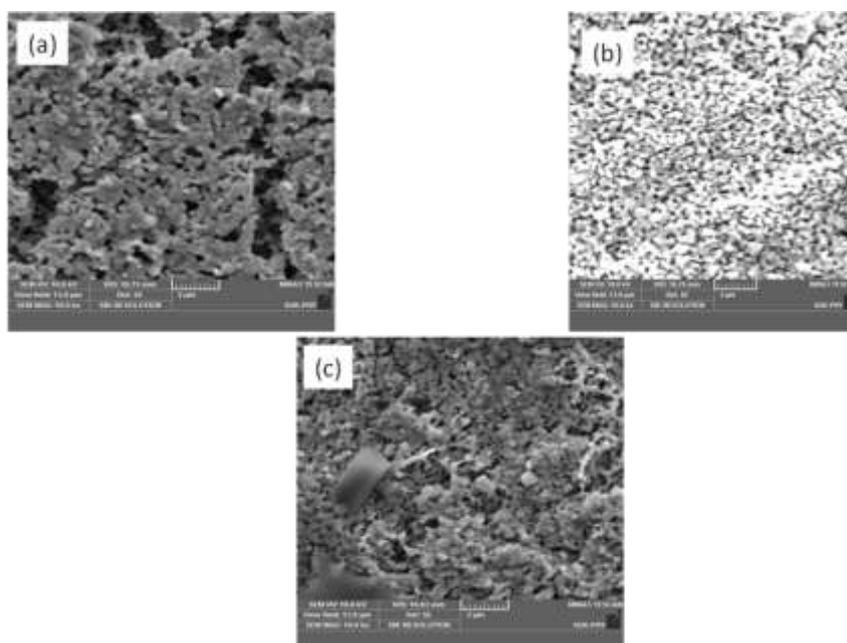


Fig.4 The FESEM images of LSC thin films a) X=0.1, b) X =0.2, c) X =0.3

3.4 Conductivity of LSC thin films:-

Fig. 5 depicts the D.C. conductivity versus reciprocal of temperature for various strontium concentrations. It is found that as strontium content increases the magnitude of D. C. conductivity increases due to increased Co^{4+} content which resulted from the substitution of La^{3+} by Sr^{2+} . Further, it is observed that as temperature of LSC thin film increases the conductivity also increases and it is semiconducting nature.

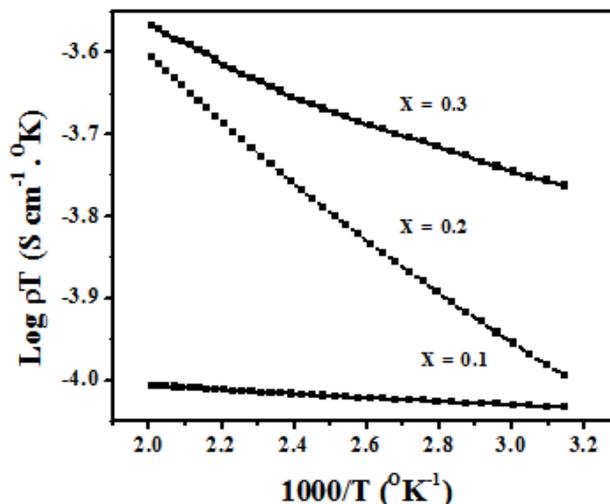


Fig.5. Conductivity of LSC films

3.4 Dielectric Constant:

As shown in fig. 6 the values of dielectric constant are very high at low frequencies. The phenomenon has been understood on the basis of space charge polarization due to the presence of porosity. Initially dielectric constant values for a LSC samples showed a sharp decrease and after decrease was found to be slow and became almost constant up to frequency 1MHz. This observed trend of decrease in dielectric constant with increased frequency may be attributed to the inability of the electric dipoles to be influenced by the applied field and due to interfacial polarization. The higher dielectric constant at lower frequencies is associated with heterogeneous conduction in composites, but sometimes the polaron hopping mechanism results in electronic polarization contributing at low frequency dispersion [2]. According to Koops theory [10] the dielectric constant attain a large values in the system is related to grains and interfaces presented in that material.

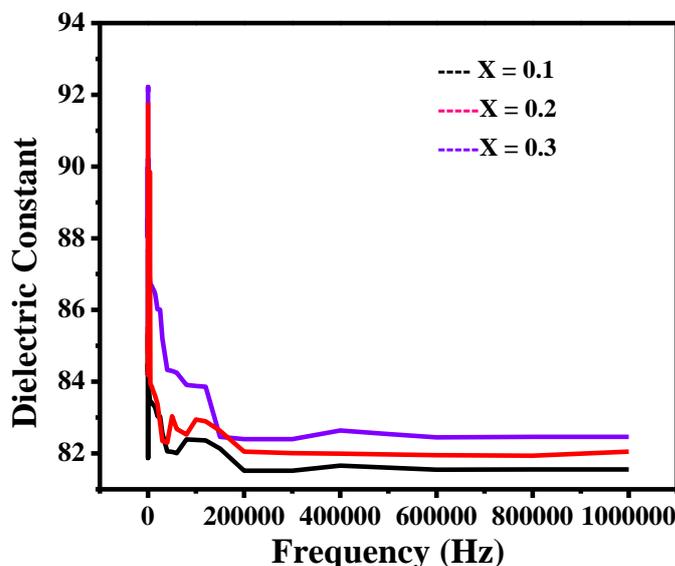


Fig.6. Dielectric Constant Vs frequency

IV. Conclusion

Lanthanum Strontium Cobaltite ($\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3.8}$) thin films as cathode for solid oxide fuel cell were synthesized by spray pyrolysis technique successfully. The porous LSC thin film after sintering at 1000°C , are usable as cathode for solid oxide fuel cell. The XRD analysis confirms the perovskite structure having unit cell is rhombohedral with space group $R\bar{3}C$. The FESEM images confirm the porous microstructure of LSC thin films which is more suitable for SOFC cathodes. As temperature increases the D.C. conductivity increases and it is semiconducting behavior of the samples.

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