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Short Communication

# Electrochemical Characteristics of La<sub>0.65</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> and La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> Nanoceramic Cathode Powders for Intermediate Temperature Solid Oxide Fuel Cell (SOFC) Application

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In the present investigation,  $La_{0.65}Sr_{0.3}MnO_3$  (LSM-1) and  $La_{0.8}Sr_{0.2}MnO_3$  (LSM-2) nanoceramic powders were prepared by the citrate-nitrate route of auto-combustion with citrate to nitrate (c/n) ratio : 0.50 to assess the effect of these cathode powders on the performance of single SOFC cells. The prepared powders were calcined at 900 °C for 4hrs to remove carboneous residues and characterized them using SEM / EDS, XRD, TGA techniques. The electrochemical characterization of LSM cathode powders were carried out by coating these powders (as cathode functional layer CFL-Bottom and current collector layer CL-Top) using screen printing on the SOFC half cells (NiO-YSZ+YSZ) procured from CGCRI, Kolkata, India with a cell size of 36 mm dia x1.6 mm. These cells were tested with H<sub>2</sub>-O<sub>2</sub> at 700-800 °C with the flow rates of 1.2-1.8 L min<sup>-1</sup> of hydrogen and 0.4-0.6 L min<sup>-1</sup> of oxygen. The current density and powder density values obtained for SOFC single cells were 0.85 A cm<sup>-2</sup> (at 0.7 V) and 0.58 W cm<sup>-2</sup> at 800 °C with 1.8 L min<sup>-1</sup> hydrogen and 0.60 L min<sup>-1</sup> oxygen. The area surface resistance (ASR) values obtained were ~0.52-0.58  $\Omega$  cm<sup>2</sup> at 0.7 V at 800 °C.

**Keywords:** Strontium-doped lanthanum manganite, Solid Oxide Fuel Cell, Nickel anode, Yttria-stabilized zirconia, Cathode functional layer, Current collector layer

#### **1. INTRODUCTION**

The Solid Oxide Fuel Cells (SOFCs) are one of the prominent candidates for power generators that convert chemical energy directly into electricity, with high efficiency and causing little pollution [1,2]. However, the commercialization of SOFC technology is hindered due to the high cost involved. For an economically viable system, better materials have to be developed to meet the challenges. The  $La_{0.8}Sr_{0.2}MnO_3$  (LSM) is a classical cathode material for SOFC based yttria-stabilized Zirconia

electrolyte, because of its high electrical conductivity, excellent thermal properties/tolerance, and chemical stability band compatibility with ZrO<sub>2</sub> based electrolyte at the working temperatures of 800-1000 °C. The cathode for O<sub>2</sub> reduction is an important area for SOFC development since its performance is often dominated by cathode polarization, which mainly occurs at lower operating temperatures where inexpensive materials may be used for the components of SOFC. There are several methods used in the production of LSM powders, such as solid phase synthesis, sol-gel and electrochemical synthesis methods [3-6]. Ze Liu et al [7] studied LSM-infiltrated LSCF cathodes for anode supported solid oxide fuel cells at 825 °C, obtaining a power density of ~1.07 W cm<sup>-2</sup> and about 24% higher power output than without LSM infiltration, as well as little degradation in cell performance over a period of 100 hrs. The current status of the development of a SOFC cell unit is based on yttria-stabilized zirconia (YSZ) solid electrolyte and electrodes consisting of Sr-doped LaMnO<sub>3</sub> (Cathode) and Ni-YSZ cermet (Anode) [8,9]. Although LSM is an excellent cathode material for high temperature SOFC due to its good stability, high catalytic activity toward oxygen reduction and excellent compatibility with YSZ electrolytes. It becomes less efficient when the cell operating temperature is reduced due to its low electronic and ionic conductivity, leading to a drastic decrease in active sites beyond the three-phase-boundary [10,11].

In recent years, several researchers have attempted to use  $La_{0.65}Sr_{0.3}MnO_3$  with 50% YSZ as a cathode function layer to enhance the cell performance [12,13]. Pal et al [12] have prepared  $La_{0.65}Sr_{0.3}$  MnO<sub>3</sub> with L-alanine to nitrate ratio of 1:1 using the auto-ignition process, studying their thermal and electrical and electrochemical properties at 600-800 °C. Haanappel et al [13] studied the optimization of processing and microstructural parameters of LSM cathodes to improve the performance of anode supported SOFCs. The current density values, they obtained were 1.5 A cm<sup>-2</sup> at 0.7 V with LSM:YSZ ratio of 50:50 by wt % at 800 °C. Buchkremer et al [14] tested a double layered  $La_{0.65}Sr_{0.3}$  MnO<sub>3</sub> (LSM) / LSM-Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ) cathode applied on a thin YSZ and operated between 800-1000 °C. The current density of 0.5 A cm<sup>-2</sup> at 750 °C at 0.7 V was achieved.

The present investigation attempts to study the effect of combination of  $La_{0.8}Sr_{0.2}MnO_3$  and  $La_{0.65}Sr_{0.3}MnO_3$  cathode powders on the performance of the scaled up SOFC cells of size 36 mm dia. This study uses the CFL (50wt%  $La_{0.65}Sr_{0.3}MnO_3$ -50wt%YSZ) as cathode functional layer and CL ( $La_{0.8}Sr_{0.2}MnO_3$ ) as current collector layer. The physical and electrochemical characteristics of the above powders in single cells at 700-800 °C using H<sub>2</sub> and O<sub>2</sub> were investigated in a specially designed and fabricated fuel cell test station and data collected to draw I-V and I-P curves.

#### 2. EXPERIMENTAL

# 2.1 Preparation of La<sub>0.65</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (LSM-1) and La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM-2) nanoceramic powders

The  $La_{0.65}Sr_{0.3}MnO_3$  (LSM-1) and  $La_{0.8}Sr_{0.2}MnO_3$  (LSM-2) nano ceramic powders were prepared by auto-combustion technique [15-17] using appropriate required amounts of  $La(NO_3)_3$ .6H<sub>2</sub>O(BDH), Sr(NO<sub>3</sub>)<sub>2</sub>, and Mn(CH<sub>3</sub>COO)<sub>2</sub>. 4H<sub>2</sub>O, citric acid (BDH), and distilled water. The precursor solution was prepared by mixing individual aqueous solution with the above chemicals with 99.0 % purity. Then required citric acid was added to the nitrate solutions and mixed properly until a clear solution was obtained without any precipitation in the pyrex glass. The citrate / nitrate ratio maintained was 0.50. The pyrex glass beaker with the solution was heated to evaporate on a hot plate at 250 °C using a magnetic stirrer until a chocolate colored gel was formed. When the heating was continued, the gel was completely burnt, enabling a light, fragile ash to be obtained. The ash was then calcined at 900 °C for 4hrs in a Barnstead Thermolyne 47900 Furnace (USA). Figure 1 shows the flow Sheet for the preparation of LSM Powders by auto-ignition technique. Table 1 shows LSM powder samples prepared and Table 2 shows the physical properties of yettrium stabilized zirconium oxide (YSZ) powder [18].



**Figure 1.** Flow Chart for preparing of La<sub>0.65</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (LSM-1) and La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM-2) cathode nano ceramic powders by auto-ignition Technique [ 18-20].

LSM-1 Cathode	Cathode Functional Layer	LSM -2 Cathode current
Sample ID	(CFL)	collector Layer
243a, 243b		(CL)
		Sample ID # 201a , 201b
-	50% LSM-1 + 50% YSZ	
	[Inter Layer]	-
La <sub>0.65</sub> Sr <sub>0.35</sub> MnO <sub>3</sub>		La <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub>
<i>C</i> / <i>N</i> : 0.75		<i>C</i> / <i>N</i> : 0.50
		[Top Layer over CFL]

Table 1. Batches of cathode LSM nano ceramic powders prepared by auto-ignition technique.

a: as prepared, b: calcined at 900°C for 4 hrs.

Table 2. Properties of Tosoh Yttrium Stabilized Zirconia powder - YSZ [21].

S.no	Physical Characteristics	Value
1	Crystallite size nm	25
2	Particle size D50 µm	0.6
3	Granule size D50 µm	60
4	Bulk density g cm <sup>-3</sup>	1.3
5	Surface area m <sup>2</sup> g <sup>-1</sup>	16
6	Loss of ignition (1000 °C) wt %	1.5

#### 2.2 SEM / EDS Characterization

Small amounts of the samples were spread on adhesive conductive aluminum tapes attached to sample holders, coated with thin films of gold and examined by the Scanning Electron Microscope. The equipment used for analysis was JEOL-JSM-6010Plus / LV Scanning Electron Microscope, Japan. The microscope was equipped with an energy dispersive X-ray Analyzer (EDX) analysis system. The Scanning Electron Microscope operated at 20 KV. The energy dispersive X-ray Analyzer (EDX) was used to determine the elemental compositions and their distribution at area and spot on polished cross section of the full fuel cells. Imaging was performed in Secondary Electron (SEI) mode only, using an accelerating voltage of 20 keV.

# 2.3. XRD Characterization

(i) A part of the samples were analyzed by the X-Ray Diffractometry (XRD) System. The crystalline phases of the samples were examined for phase characterization by X-ray diffraction analysis MiniFlex; Rigaku, Japan. The X-ray Diffractometry with CuK $\alpha$  radiation at 40KV and 35mA was used for phase analysis with in a diffraction angle 2 theta range 10-70 ° and particle size determination from X-ray line broadening technique using the following Debye Scherrer Eq. (1) [19]:

 $t = 0.9\lambda / B \cos \emptyset \tag{1}$ 

where t = Average crystallite size in nm,  $\lambda$  = the wave length (0.15418 nm) of Cu K $\alpha$  radiation, B the width (in radian) of the XRD diffraction peak at half of its maximum intensity (FWHM), where Ø is the Bragg diffraction angle of the line, and B is the line width at half peak intensity. (ii) For comparison to find approximate average particle size was found using the following Eq. (2) [20]:

DBET: 6 / (SBET x dth)(2)

where DBET is the average particle size in nm, SBET Surface area in  $m^2 g^{-1}$  and dth is the theoretical density of the material in g cc<sup>-1</sup> [assuming that the particles have spherical shape and uniform size].

#### 2.4. Surface Area Characterization

The surface area of samples was measured using an Autosorb-1C instrument manufactured by Quanta Chrome, USA. Samples were taken in the range of 0.1 - 0.2 g in a cell and were degassed at 300 °C for 3 hrs to remove any absorbed material on the surface. Nitrogen gas was used as the adsorbent. The surface area (m<sup>2</sup> g<sup>-1</sup>) of the prepared powder and after calcined powder at 900 °C have been calculated.

#### 2.5. TGA Characterization

In order to determine the decomposition behavior of the LSM samples, around 7-8 mg of the samples were loaded in a alumina crucible and put inside the thermo balance of TG Machine (Perkin-Elmer Thermal Analysis). The thermal decomposition behavior was studied up to 800 °C. The half cells of SOFC with 36 mm dia and 1.5 mm thick with NiO-YSZ 1.5 mm thick and YSZ that was raised at a rate of ~10 °C per minute. The Thermal Gravimetric Analysis (TGA) of LSM-1 and LSM-2 powder plots are presented.

#### 2.6 Electrochemical Characterization

#### 2.6.1 SOFC Half Cells (36 mm dia x 1.5mm) Procured from CGCRI, Kolkata, India

The NiO-YSZ +YSZ half cells of 36 mm dia x1.5 mm thick were procured from CGCRI, Kolkata, India on commercial bases. The anode (NiO-YSZ) has a thickness of 1.5 mm and the electrolyte (YSZ) thickness was around 15 microns. These half cells (NiO-YSZ-YSZ) were fabricated with tape casting technique to prepare anode (NiO-YSZ) and electrolyte (YSZ) layers. They were then laminated and pressed at room temperature and subsequently co-sintered at 1,400 °C for 6 hrs at a rate of  $1^{\circ}$ C h<sup>-1</sup>. The details of the electrode fabrication (half cells) process are described in the references [21, 22].

# 2.6.2 Preparation cathode functional Layer (CFL) Paste (LSM-1 + 50% YSZ) and cathode catalyst Layer (CL) Paste (LSM-2)

The milled powders of CFL and CL were weighed separately and prepared as pastes to apply on the half cells. The cleaned agate bowl and grinder were wiped with isopropyle alcohol / acetone with tissue paper. Taken 10 g of cathode active layer (cathode function layer-CFL) powder and 10 g catalyst powder LSM-2 were taken into two agates separately with 2 g of binder (ethyle cellulose) with 20-25 drops of thinner (terpinol) and mixed thoroughly for 2 hrs to create a homogeneous paste. The thinner was added every half an hour. The two pastes were collected in two small bottles.

## 2.6.3 Screen printing of the CFL and CL layers on the NiO-YSZ half Cells

The CFL layer (1 layer of 10-15 microns) was first printed over the YSZ surface of half cell then dried for 30 minutes. Then 3 layers (~ 30 - 40 microns) of LSM-2 cathode paste successively over the dried CFL layer using the screen printer –SKYHILL Ming Tai Screen Printing Machine Co Ltd, China. After the screen printed half cells had dried, they were placed on a dense alumina plate and put into the furnace covered with another plate. They were then sintered at 1,050 °C for 4 hrs by heating from room temperature to 600 °C (1 hrs) at 75 °C h<sup>-1</sup> and then up to 1,050 °C at 100 °C h<sup>-1</sup>, then cooled down at 150 °C h<sup>-1</sup> to room temperature. At this point, the full cell was ready for testing in a fuel cell test station, as shown in Figures 2 and 3.



Figure 2. Scheme of SOFC single cell assembly-36 mm dia Cells (NiO-YSZ-YSZ + CFL+CL).



Figure 3. Single cell components-cathode screen printed cells (of 22 mm dia with CFL and CL) A: NiO-YSZ (anode), B: YSZ (Electrolyte), C: NiO-YSZ + YSZ (Anode+Electrolyte), D: NiO-YSZ +CFL+CL layers, [C: The Half Cells were Procured from CGCRI, D: CFL and CL layers were screen printed by with KACST LSM powders].

#### 2.6.4 Description of Experimental Set-up for testing and assembly of 36 mm dia SOFC Cells

The Test Station to evaluate single SOFC cells was procured from CGCRI (Central Glass Ceramic Research Institute), Kolkata, India. It is designed and fabricated by CGCRI. It is similar to the SOFC test stations and configurations reported by other researchers [23,24]. A brief description of the test station is given in the following paragraph:

It has a vertical furnace with two compartments, containing anode and cathode with alumina tubes with gas supply arrangements Mass Flow Controllers (MFC) for argon, hydrogen and oxygen gases. The Agilent multi meter 34401A and D.C. the Electronic Load Bank is connected to the system to measure the cell voltage and current of the cell. A Humidifier with glass balls around ~60 nos with 5 mm dia and water of 70 ml is fixed before hydrogen enters the cell (Figures 4). The cell is loaded vertically. Hydrogen gas is passed from the bottom of the anode compartment and oxygen gas is passed from the top of the cathode compartment. A single cell of 36 mm dia x 1.6 mm thick is placed between two Alumina tubes with a current collector with platinum mesh, so the effective electrode is considered as 1.13 cm<sup>2</sup>, which corresponds to a printed diameter of 22 mm. Single cells configurations NiO -YSZ / CFL/ CL were then evaluated for their electrochemical performance. The anode side NiO-YSZ is faced toward the hydrogen gas and CFL+CL screen printed over the electrolyte of the half cell faced towards the oxygen gas.



Figure 4. Schematic of experimental set-up to test 36 mm dia SOFC Single Cells

The cell is sealed using glass rings that melt at 1000 °C. The furnace temperature is then brought down to 800°C with temperature controller M/S A.G.Enterprise ,West Bengal, India. Argon and hydrogen are purged in the anode chamber and simultaneously the voltage is recorded. The purging and simulations gas switches from argon to hydrogen and oxygen in the anode and cathode compartments, which are kept on until the voltage reaches an open circuit voltage (OCV) of 1.10 V. The electrochemical performance can be evaluated using variable flow rates of fuel – hydrogen and oxidant - oxygen viz. 1.8 L min<sup>-1</sup> H<sub>2</sub> and 0.6 L. min<sup>-1</sup> O<sub>2</sub> respectively. The electrochemical performance is recorded using DC Electronic Load Bank for current and Agilent Digital multi meter for cell voltage in the temperature range of 700-800 °C at an interval of 50 °C . I-V and I-P curves are plotted with varying gas flow rates with H<sub>2</sub> (1.2-1.8 L min<sup>-1</sup>) and with O<sub>2</sub> (0.4-0.6 L min<sup>-1</sup>).

# **3. RESULTS AND DISCUSSION**

# 3.1 Physical characterization

## 3.1.1 SEM / EDX

Figure 5 shows the SEM images for calcined and milled LSM-1 powders. It can be seen that the oxide particles are well crystallized, with a clear shape, and that the particle dia is less than 300 nm [25]. The powders were milled for 24 hrs under ethanol media, with  $ZrO_2$  balls of size 5 mm dia. and dried at 100 °C for the preparation of the CFL before application on the half cells of 36 mm dia. The properties of YSZ powders are given in Table 2.



Figure 5. SEM of La<sub>0.65</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> LSM-1 [After Milling for 24hrs].



Figure 6. SEM of CFL-1(LSM-1+50% YSZ) Powder after being milled for 24hrs.

Figure 6 shows the CFL powder after being milled for 24 hrs using  $ZrO_2$  balls of 5 mm dia. It can be seen to have a fine structure, with fine particles of less than 200 nm.

Figure 7a and Figure 7b show the SEM image of LSM-2 powders that were calcined and milled for 24 hrs respectively, indicating the particle size reduction ranging from around 200-300, nm with a slight agglomeration. Figure 8a and Figure 8b show the EDS plots of the LSM-2 and LSM-1 powders, along with the qualitative amounts of elements present in the powders as shown in Table 3.



Figure 7a. SEM of LSM-2 Calcined at 900 °C for 4hrs.



Figure 7b. SEM of LSM-2 calcined and milled powder.



Figure 8a. EDS pattern of LSM-2 powder calcined at 900 °C for 4hrs.



Figure 8b. EDS pattern of LSM-1 calcined and milled for 24hrs.

**Table 3.** the weight % of the elements in LSM-1 and LSM-2.

Component	Weight %				
	La	Sr	Mn	С	0
$La_{0.8} Sr_{0.2} MnO_3$ [Calcined]	41.9	7.4	18.0	9.30	23.3
$La_{0.65}$ Sr <sub>0.3</sub> MnO <sub>3</sub> [Calcined]	32.9	15.6	20.3	10.3	20.8

#### 3.1.2 TGA Characterization

Figures 9a and 9b show the thermal analysis of as prepared LSM nano powders in the range of 30-900 °C. It can be seen from the TGA plots of LSM-2 and LSM-1 that the drastic weight loss occurred at about 220 °C for both the powders. The weight loss was found to be 10.46 g and 4.12 g for the prepared LSM-2 and LSM-1 respectively. After an initial small weight loss of adsorbed water at 160 °C, indicating decomposition of metal-citrate complexes and formation of crystalline phase of the LSM powders, No further weight loss was observed after a temperature of ~600-650 °C was reached in the TGA plots, indicating completion of combustion. The thermal behavior of both the powders are found to be similar in nature. Similar trends have been reported elsewhere for LSM powders [ 26,27].



Figure 9a. TGA Plot of LSM-2 (as prepared) powder #201.



Figure 9b. TGA Plot of LSM-1 (as prepared) powder #242.

#### 3.1.3 XRD characterization

Figure 10a and Figure10b show the XRD patterns of the LSM-2 and LSM-1 respectively . These were calcined powder at 900  $^{\circ}$ C and milled for 24 hrs under the isopropanol medium . It can be seen that the peaks obtained are similar to those reported by other authors [28,29]. It can be seen that small amounts of Mn<sub>3</sub>O<sub>4</sub> is present which might come from the change of oxidation state of the Mn ion. The crystallite size of the LSM-2 powder was 15.2 nm and the LSM-1 powder was 14.99 nm (Table 4). The powder obtained after calcination at 900  $^{\circ}$ C was pure and is reasonably comparable with the finding of other authors [26]. Table 4 shows the XRD data to determine the average crystallite size of LSM-1 was found to be around 16 nm. It can be seen that the milled powder of LSM-1 have little bit smaller crystallite size of 15 nm.



Figure 10a. XRD patterns of LSM-2 powder (calcined).



Figure 10b. XRD patterns of LSM-1 powder, calcined and milled.

Sample	With CuKa Radiation			
ID Number		$\lambda (\mathrm{Co}) = 0.15418 \mathrm{nm}$		
	В	Crystallite size,		
	FWHM	t (nm)		
201b [LSM-2] (Calcined at 900 °C for 4hrs)	0.54868	15.20		
242 b [LSM-1] (Calcined at 900 °C for 4hrs)	0.5211	15.88		
242 b [ LSM-1](Calcined milled for 24 hrs)	0.5522	14.99		

<b>Table 4.</b> AND Data to determine the average crystallite size of the LSW po	RD Data to determine the average crystallite size of the LSM	powders.
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Average crystallite size = t = 0.9 x  $\lambda$  / B Cos Ø , B= FHHM in °,B =[FWHM x 22/7 ÷ 180 ]= FWHM x 0.017460

#### 3.1.4 Surface area characterization

Table 5 shows the surface area of the prepared and calcined LSM powders respectively. The surface area for the prepared powder was 23.48 m<sup>2</sup> g<sup>-1</sup> and 21 m<sup>2</sup> g<sup>-1</sup> calcined powder at 900 °C. The surface area reduced after calcination of LSM-2 nano powder there by increased in particle size as per expectation. The surface area of LSM-2 achieved for the calcined powder was greater than previously reported [28]. It can be seen that the approximate average crystalline size calculated from specific surface area d<sub>BET</sub> of the prepared and calcined LSM powders were 38.65 nm and 48.9 nm, respectively, assuming the theoretical density of LSM 6.521 g cc<sup>-1</sup> using Eq (2) [19,25] and assuming spherical particles. It can be seen that the average particle size value d<sub>XRD</sub> value of 15.2 nm was obtained from XRD data using Debye Scherrer equation. The d<sub>BET</sub> and d<sub>XRD</sub> values are comparable with extant studies [28].

	Table 5. Surface area data and	l average crystallite s	size of $La_{0.8}Sr_{0.2}MnO_3$ (	(LSM-2) powders.
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Sample	Surface Area ( $m^2 g^{-1}$ )	Average crystallite size	Average	$d_{BET}/d_{XRD}$
ID Number	Multipoint BET	with	crystallite size	
		$d_{BET} = 6/ [d_{th} \times S_{BET}]$	with XRD	
		[ 23, 31] nm	d <sub>XRD,</sub> nm	
201b [LSM-2]	21.00	43.81	15.20	2.88

 $D_{BET}$  = average crystallite size,  $d_{th}$  = theoretical density of LSM ( 6.521 g cc<sup>-1</sup>) ,  $S_{BET}$  = surface area(  $m^2 g^{-1}$ )

# 3.2 Electrochemical characterization of SOFC single Cell.

Figures 11a - 11c show the I-V and I-P curves for the single SOFC cell [# 201] with three flow rates 1.2 - 1.8 L min<sup>-1</sup> of hydrogen and 0.4-0.6 L min<sup>-1</sup> of oxygen at three operating temperatures (700, 750, 800 °C) using 3% of humidified hydrogen gas. The OCV values for the cells were approximately 1.08-1.09 V, indicating that a dense electrolyte structure is well-formed on the NiO-YSZ surface so that the leakage is negligible. Figure 11a illustrates that the maximum current density

(cd) obtained is around 0.66 A cm<sup>-2</sup> at a cell voltage of 0.7 V and the power density (pd) is around 0.506 W cm<sup>-2</sup> at 800 °C with H<sub>2</sub> and O<sub>2</sub> flow rates of 1.2 L min<sup>-1</sup> and 0.4 L min<sup>-1</sup> respectively. However, when the cell operating temperatures were reduced to 750 °C and 700 °C, the cd and pd values fell to 0.44 A cm<sup>-2</sup> and 0.31 A cm<sup>-2</sup> and 0.3 W cm<sup>-2</sup> and 0.22 W cm<sup>-2</sup>, respectively. This reduction in reaction rates occurred due to low temperatures as the ASR values (Table 5) obtained were increased to 0.834-1.0 2  $\Omega$  cm<sup>2</sup>, which are higher than the accepted values (~less than 0.5  $\Omega$  cm<sup>2</sup>) for SOFC applications.



Figure 11a. Current –Voltage (I-V) curves and current-power (I-P) curves of an anode supported SOFC single cell # 243 with different temperatures (700-800  $^{\circ}$ C) and flow rates (H<sub>2</sub>: 1.2 and O<sub>2</sub>: 0.4 L min<sup>-1</sup>).

Figure 11b shows the I-V and I-P curves for the single SOFC cell [# 201] with the flow rates of  $1.5 \text{ L} \text{min}^{-1}$  of hydrogen and 0.5 L min<sup>-1</sup> of oxygen at the temperatures 700-800 °C with the same 3% of humidified hydrogen gas. It can be seen from Figure 11b that the maximum current density obtained is around 0.71 A cm<sup>-2</sup> at a cell voltage of 0.7 V and the power density is around 0.53 W cm<sup>-2</sup> at 800 °C. It is clear that the cd and pd values increased slightly with increasing gas flow rates to 1.5 L min<sup>-1</sup> of hydrogen and 0.5 L min<sup>-1</sup> of oxygen. Similar results were observed when the cell operating temperatures were reduced to 750 °C and 700 °C, as the cd and pd values declined to 0.54 A cm<sup>-2</sup>, 0.38 W cm<sup>-2</sup> and 0.33 A cm<sup>-2</sup> 0.24 W cm<sup>-2</sup>, respectively.



**Figure 11b.** Current –Voltage (I-V) curves and current-power (I-P) curves of an anode supported SOFC single cell # 243 with different temperatures (700-800 °C) and flow rates (H<sub>2</sub>: 1.5 and  $O_2$ : 0.5 L min<sup>-1</sup>).

Figure 11c shows the I-V and I-P curves for the single SOFC cell [# 201] with the flow rates of 1.8 L min<sup>-1</sup> hydrogen and 0.6 L min<sup>-1</sup> oxygen at 700-800 °C with the same 3% of humidified hydrogen gas. Figure 11c shows that the maximum current density obtained is around 0.83 A cm<sup>-2</sup> at a cell voltage of 0.7 V and the power density is around 0.58 W cm<sup>-2</sup> at 800 °C. However, when the cell operating temperatures were reduced to 750 °C and 700 °C, the cd and pd values were also lowered to 0.655 A cm<sup>-2</sup> and 0.4 W cm<sup>-2</sup> and 0.43 A cm<sup>-2</sup> and 0.28 W cm<sup>-2</sup>, respectively.



**Figure 11c.** Current –Voltage (I-V) curves and current-power (I-P) curves of an anode supported SOFC single cell # 243 with different temperatures (700-800  $^{\circ}$ C) and flow rates (H<sub>2</sub>: 1.8 and O<sub>2</sub>: 0.6 L min<sup>-1</sup>).

At the lower temperatures (700-750 °C) the cd and pd values are low which may be due to several reasons like YSZ content in the CFL, or its thickness being greater than planned (~18 microns) as it was screen printed manually. However, the cd and pd values obtained for the single SOFC were 0.83 A cm<sup>-2</sup> and 0.58 W cm<sup>-2</sup> at the gas flow rates flow rates 1.8 L min<sup>-1</sup> hydrogen and 0.6 L min<sup>-1</sup> oxygen respectively at the operating temperature of 800 °C, with the combination of LSM-2 as CL and LSM-1 with 50% YSZ as CFL over the YSZ electrolyte. These results obtained in the present work are in agreement with other researchers reported [23,30]. There may be several reasons for reductions observed in the current density and power density, such as starvation of fuel and lowering reaction kinetics at the cathodes, especially at low temperatures of 700-750 °C. It is therefore planned that special cathode materials like CGO-LSCF be developed, using different anode functional layers to obtain higher output power at lower temperatures ~700 °C, as reported by Moon et al [30].

Table 6 shows the summary of the results of current density, power density and linear plots for area surface resistance (ASR) values at the temperatures 700-800 °C. The values obtained (~0.52  $\Omega$  cm<sup>2</sup>) at 0.7 V, 800 °C in the present work are quite comparable and support the finding of other authors [30-32]. Therefore, such cells can be used with combination of LSM-1 and LSM-2 as cathode materials for low temperature (800 °C) SOFCs applications. There are multiple parameters of the anode side that can affect the performance of the single cells, such as microstructure, pore / pore size distribution, three phase boundary, anode electrolyte interference, and anode thickness. These parameters can lead to outcomes that include Ohmic polarization of anode/electrolyte interference or the concentration / activation polarization of electrodes, in turn yielding a reduction of overall cell voltage of cells.

Flow rates	Operating	Current density	Power density	ASR
$(L \min^{-1})$	Temp. <sup>o</sup> C	$mA cm^{-2}$	$mW cm^{-2}$	$\Omega \text{ cm}^2$
	700	308	219	1.02
$H_2: 1.2$	750	442	307	0.988
$O_2: 0.4$	800	660	506	0.834
	700	330	236	0.994
$H_2: 1.5$	750	540	380	0.707
$O_2: 0.5$	800	708	527	0.578
	700	430	280	0.908
$H_2: 1.8$	750	655	401	0.558
$O_2: 0.6$	800	830	580	0.518

Table 6.	Current density,	power densit	y and Area	surface	resistance	(ASR )	) values.
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Figures 12 a -12b show the SEM micrograph of the anode surface and cross section of the SOFC single cell showing the different layers of CFL and CL, YSZ and NiO-YSZ. The YSZ electrolyte with 13 microns is supported by the anode with 1.5 mm in thickness. The YSZ layer was essentially dense and uniform, with no open pin holes. It had continuous and crack free surface

morphology. It can be seen that both the anode and cathode layer were well-adhered to the electrolyte layer. It can also be seen that the thickness of CFL and CL are marginally greater, which may also contribute to the lowering of the power output, especially at lower temperature cell operations. This is particularly true as the resistance increases, with the increasing thickness of the layers. Reducing the % YSZ content in the CFL layer, lowering CL layer thickness and introducing an anode functional layer, as studied by Moon et al [31], may yield better performance of the SOFC cells. The work is in progress on these lines and will be communicated in our future publications.



Figure 12 a. SEM micrographs of anode surface.



Figure 12 b. SEM micrographs of cross section of SOFC Single Cell after testing at 800 °C.

# 4. CONCLUSIONS

The following conclusions are drawn from the present work:

(i) The LSM-1 and LSM-2 nanoceramic cathode powders were prepared using autoignition technique with c/n: 0.75 with average crystallite size of 15-16 nm by Deby Scherrer equation and SEM images indicate particle size of the LSM powders indicate about 300 nm.

(ii) TGA plots for LSM as prepared powders indicate no weight change after 600  $^{\circ}$ C, which indicates the completion of combustion.

(iii) XRD patterns shows the formation of pure LSM powders after calcination of the ash obtained with auto- ignition at 900  $^{\circ}$ C for 4hrs.

(iv) Cathode functional layer (CFL) with 50% YSZ worked satisfactorily achieving a reasonable current density  $0.8 \text{ A cm}^{-2}$  at 0.7 V and power density 0.6 W cm<sup>-2</sup> with H<sub>2</sub>: 1.6 L min<sup>-1</sup>, O<sub>2</sub>: 0.6 L min<sup>-1</sup> using the combination of LSM-1 amd LSM-2 for CFL and CL respectively, with an electrode surface area of 1.1 cm<sup>2</sup>. However, further reducing the % of YSZ (40%) in CFL may yield higher current density and power density.

(v) The surface area of the LSM-2 powder was found to be 23.4 m<sup>2</sup> g<sup>-1</sup> and 21 m<sup>2</sup> g<sup>-1</sup> for the prepared and calcined powders respectively.

(vi) The Area surface resistance (ASR) values obtained were in the range of 0.50 - 0.55  $\Omega$  cm<sup>2</sup> at 0.7 V at 800 °C with H<sub>2</sub>: 1.8 L min<sup>-1</sup>, O<sub>2</sub>: 0.6 L min<sup>-1</sup>, for the 36 mm dia SOFC cells.

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