



Enhanced Performance of LSCF as a Cathode Material for Solid Oxide Fuel Cell By Using Gamma Radiation

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Abstract

Gamma radiation has always an impact on semiconductor material by altering its physico-chemical properties. In this paper nano sized crystallites of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) which is a promising cathode material for intermediate temperature-solid oxide fuel cells (IT-SOFCs). LSCF was synthesized by sol-gel technique and modified sol-gel technique by Gamma irradiation methods. The structure, morphology, elemental analyses and surface area were determined by X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM), scanning transmission electron microscope (STEM) analysis and Brunauer-Emmett-Teller (BET) method. Also Dc conductivity was measured from room temperature up to 500 °C. Results showed that samples synthesized by irradiation method were more porous structure, higher surface area and oxygen vacancies as compared to un-irradiated sample. So, irradiation technique has a pronounced effective role in improvement microstructure of LSCF cathode material.

Keywords: LSCF Cathodes; SOFCs; Gamma irradiation; X-ray; (BET); Perovskite; Morphol

Introduction

Fuel cells is considered as an attractive tool to generate electricity that converts energy directly from chemical to electrical form with high efficiency and lower pollutants' emission. Due to operating conditions, solid oxide fuel cells (SOFCs) are more stable against impurities in comparison with polymer electrolyte membrane (PEM) fuel cells. However, SOFCs has the disadvantages of high cost and degradation due to high operating temperature compared with PEM. For this reason, the recent research work aimed mainly on lowering the working temperature to decrease SOFCs' cost and to increase their lifetime. Studies focused also on using perovskite-type complex oxides in SOFCs due to their desirable properties, low cost and wide spectra of applications [1].

Cathode materials should have excellent electrical conductivity and electrocatalytic activity for the oxygen reduction reaction (ORR). It should have also adequate porosity to enable the transportation phenomena [2]. Although $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) perovskite used to be the best superior of cathodes for high temperature SOFCs, nowadays, its application in intermediate temperature solid oxide fuel cell (IT- SOFCs) is extremely restricted due to its very low ionic conductivity and pitiable electrocatalytic activity in the lower

temperature range [3]. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF), cathode material is the best choice for IT- SOFCs as it shows high activity, high thermal and chemical stability, high mixed electronic-ionic conductivity and high thermal compatibility with other fuel cell material [4].

Synthesis method is fundamental factor in determining and controlling the final morphology and microstructure of produced perovskite cathode materials for IT- SOFCs. To obtain good properties for these materials, several synthesis methods were developed for their preparation [5-8].

Preparing SOFCs cathode by firing ceramic grade materials at high temperature leads to lowering the surface area which in turn limits current density exchange; so, sol-gel (SG) technique is recently used as reliable method to prepare SOFCs cathode to overcome this drawback [9,10]. This method not only save time and energy but also produces highly porous structure with high surface area that is suitable for wide range of applications. Additionally, SG method has the advantages of controlling texture, composition, consistency and other essential properties of prepared materials leading to improving the structural and electrochemical properties of the developed films [11, 12]. Measuring the specific surface area of prepared perovskites cathode materials is an essential tool to determine and

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optimize their electrochemical properties and electrocatalytic activity. Brunauer- Emmett- Teller (BET) nitrogen adsorption method is used to measure the surface area values of prepared perovskites materials [13]. Properties of LSCF cathodes depend not only on strontium or cobalt contents but also on the grain sizes, porosity, oxygen vacancy concentration and on the sintering time and temperature [14]. The oxygen reduction reaction (ORR) is one of the most important electrochemical reactions in energy conversion and storage technologies, such as fuel cells and metal-air batteries. Studies have shown that the catalytic properties of perovskite oxides in the ORR are largely related to oxygen vacancies, which alter their electronic and crystal structures and surface chemistry. In addition, the presence of oxygen vacancies enables lattice oxygen to move on the perovskite surface, and reduces the barrier of oxygen migration, making it easier for oxygen to migrate into the interior of the electrode material. Therefore, oxygen vacancies play a key role in the ORR. By using scanning transmission electron microscopy (STEM) studies to characterize oxygen vacancies in perovskites have observed significant advances in describing and understanding oxygen vacancies in perovskite oxides [15]. This research work aims to studying the effect of γ -ray radiation as powerful treatment in nano particles modification on the morphology and properties of LSCF cathode material in comparison with Sol- Gel traditional technique. This is considered innovative approach and new technique for improvement performance of LSCF cathode material comparing with other studies; which used composite materials [16]. Using composite material is considered costly and take long time in preparation. The gamma radiation technique is useful and has been extensively used to generate nanoscale materials at room temperature under normal pressure. Moreover, this technique is well controlled and flexible, and it does not contribute impurities into the matter [17]. Radiation can enhance diffusion rates by producing an increased concentration of oxygen vacancy and improvement of surface mobility [18].

Experimental:

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) precursor was synthesized by two approaches:

- Sol gel route: in which the Sol-gel method was used [19]. The typical route using high purity analytical grade metal nitrates $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ From Fluka company. All these chemical salts dissolved in distilled water and urea. Then the solution was refluxed and stirred continuously at 200°C for 4 h, and concentrated to about 2/3 of its volume to get gel precursor. Thermal

degradation behavior of the LSCF was studied using the obtained precursor product to determine the temperature at which perovskite phase formed using the thermal gravitational analysis (TGA). Precursor was left overnight then calcinated at 900°C and 1100°C for 6 h in air to obtain LSCF cathode powders. Calcination process is used to remove humidity, crystalline water, and dissociation of volatile matter and formation of the LSCF crystals.

- Modified sol gel by gamma irradiation: In this process we radiated the yield product from the sol gel route before calcination by different doses of gamma irradiation (20, 250 and 500 kGy), with Cobalt 60 source (Ge 4000A). The Co-60 γ -rays source of NCCRT (India Gamma chamber 4000 A,) was used for the irradiation of the samples. The samples were subjected to γ -rays at room temperature with dose rate 1.347 kGy/h . The absorbed dose rate of the cell was calibrated using a Fricke reference standard dosimeter (ASTM E 1026, 2004) and verified by a reference alanine dosimeter (traceable to National Institute of Standard and Technology, USA). The irradiation process was carried out in the central position of the cell that was calibrated by reference standard dosimeter. Then we calcinated the radiated samples at 1100°C for 6 h.

The samples have been characterized using a fully computerized X-ray diffraction (XRD) technique using a Philips PW-1730 apparatus with $\text{Cu K}\alpha$ irradiation ($\lambda=1.5406\text{ \AA}$) in the range of $20^\circ \leq 2\theta \leq 80^\circ$ by continuous scan with tube voltage 40 kv, 40 mA and step size of 0.02° .

Thermo-gravimetric analysis was carried out on TA Q50 in nitrogen atmosphere, and the temperature-rising rate was $10^\circ\text{C}/\text{min}$. Fourier transformation infrared (FT-IR) spectroscopy was recorded on Perkin Elmer spectrum 100. Morphology of LSCF samples were observed by field emission scanning electron microscope (FESEM). Also Scanning transmission electron microscope (STEM) analysis was used to determine oxygen concentration for all LSCF samples.

Surface area and porosity measurements were carried out by BET method in nitrogen gas atmosphere under liquid nitrogen temperature.

Electrical DC conductivity measurements for LSCF samples by Hall-effect four probe technique from room temperature up to 500°C . The voltage between the two inner electrodes and the current through the sample were recorded at each temperature. The

electrical DC conductivity was calculated directly from software.

Results and Discussion :

Fig.1. Shows X-ray diffraction patterns of un-irradiated LSCF powder calcinated at 900 ° C and 1100° C. It revealed that at the calcination temperature of 900° C a minor secondary phase is present and formation of perovskite phase was not complete [19,20], but after raising calcination temperature up to 1100° C, it led to formation of pure perovskite.

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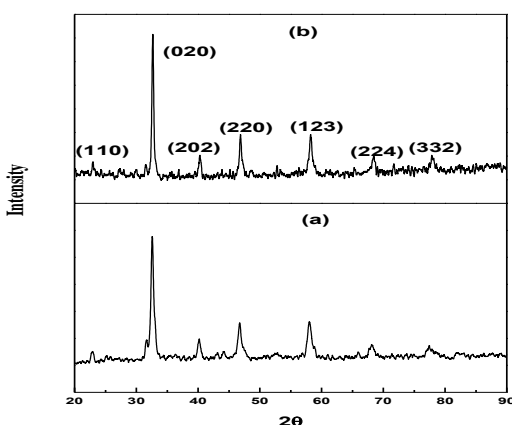


Fig.1. XRD patterns of LSCF powder as a function of calcination temperature: (a) 900°C for 6 hrs
1100°C for 6hrs

Fig.2. shows the diffraction patterns of un-irradiated and irradiated LSCF samples (20 kGy, 250 kGy, 500 kGy) after calcination at 1100 ° C for 6 h. All cases produced pure perovskite phase (JCPDS no. 48-0125) [20].

Mean crystallite size of un-irradiated and irradiated LSCF samples (20 KGy, 250 KGy,500 KGy) were determined by X-ray line broadening of diffraction patterns and the values of 19, 18, 27 and 42 nm were obtained, respectively [21].

The curves represent TGA results of un-irradiated and irradiated LSCF powder are shown in Fig.3. It shows weight changes in different stages. The maximum weight loss for un-irradiated and irradiated samples was about 45% and 50% in the temperature range 25-327° C, this loss may be due to the dehydration of the gel [22]. The loss of about ~ 20%

for un-irradiated sample and radiated one in the temperature range 327°C-540° C is correlated to nitrates. Above 540° C, no weight loss has been observed and the curves represent TGA results become horizontal. It was observed also that the weight loss in case of irradiated sample decreased in all stages. This may be due to the loss of volatile matter, humidity and crystallinity of water upon heating [22].

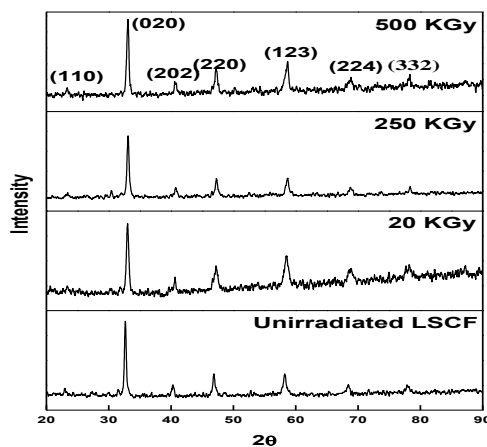


Fig.2. XRD patterns of un-irradiated and irradiated LSCF samples calcinated at 1100C for 6 hrs:

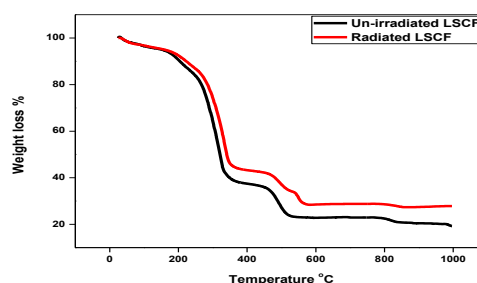


Fig.3. Thermogravimetry of LSCF samples for (a) Un-irradiated and (b) Irradiated LSCF samples

The FTIR spectra of un-irradiated and radiated LSCF samples are shown in Fig.4. The entire spectra can be divided into four main regions, from 4000 to 2500 cm^{-1} due to the stretching mode of the hydroxyl group of bound water molecules, the second region from 2500 to 2000 cm^{-1} due to ambient CO_2 , the third region from 1630 cm^{-1} and at 1385 cm^{-1} due to carboxylate, nitrate groups respectively and the fourth region due to absorption peaks which appear below 800 up to 400 cm^{-1} are caused by the different kinds of metal oxygen bonds present in the sample which are characteristics peaks for perovskite;

whereas, the absorption peaks appearing beyond 800 cm^{-1} are due to the different kinds of organic ligands [23]. It is also observed that band of hydroxyl group of water molecules bond increased; which appears around 4000 cm^{-1} . Also sharp intensity of nitrate absorption peak was observed at 1380 cm^{-1} for 20 KGy. This sharp absorption band of nitrate bond and wide water bond increases due to higher formation of oxygen vacancies than other samples [24, 25].

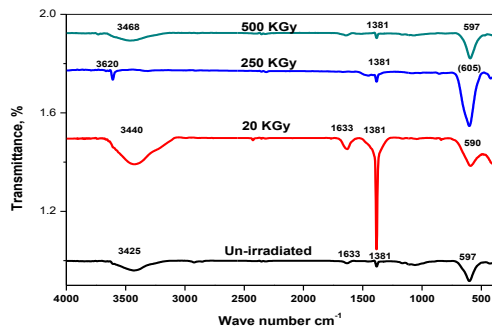


Fig.4. FTIR of un-irradiated and irradiated LSCF samples calcined at $1100\text{ }^{\circ}\text{C}$ for 6 hrs.

Morphology and microstructure analysis

The specific surface area of the samples was measured by BET technique. It was showed that, higher value of surface area and porosity for radiated LSCF sample at 20 kGy as shown in Table 1, which is considered sufficient for the cell's operation as the optimum porosity is reported to be around 20–40% [26].

Table.1. BET surface area and porosity measurements for all LSCF samples

Item	Un-irradiated LSCF	Radiated LSCF		
		20 KGy	250 KGy	500 KGy
Surface area, m^2/g	62.943	74.560	50.046	52.342
Total pore volume, cc/g	2.196×10^{-2}	2.589×10^{-2}	1.787×10^{-2}	1.843×10^{-2}
Porosity (%)	23	26	18.5	21.5

Fig.5. Shows FESEM microstructure of un-irradiated and irradiated LSCF powder that are calcinated at $1100\text{ }^{\circ}\text{C}$ for 6h. It was observed that the un-irradiated sample has a bulky structure while irradiated samples (20 KGy, 250 KGy and 500 KGy) have more refined structure. Among irradiated

samples, 20 KGy sample has the more refined grains with more surface area and more total pores size. This means that the LSCF sample radiated at low dose 20 kGy has higher porosity than other samples; which would benefit ORR due to the availability of more active sites [27].

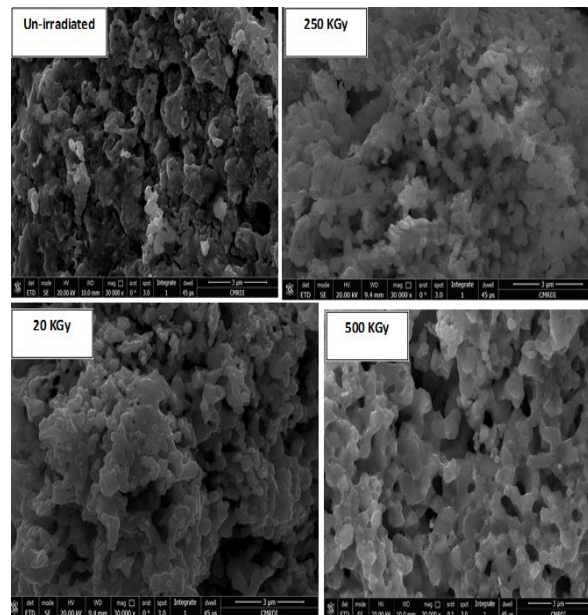
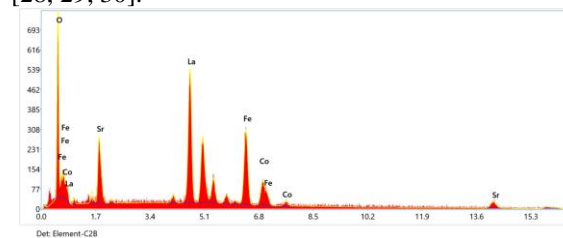


Fig.5. FESEM of Un-irradiated and irradiated LSCF samples (20 kGy, 250 kGy and 500 kGy) calcined at $1100\text{ }^{\circ}\text{C}$ for 6 hrs.

STEM examination for observing oxygen vacancies for all samples were shown in figure 6 and as tabulated in table 2. Irradiated sample at 500 KGy sample has high oxygen vacancies. This observation contrvercing our study because at 20 KGy; we showing high porosity and surface area (from BET and FESEM). It is clear that too many oxygen vacancies do not apparently benefit the ORR. The best ORR performance is often obtained from those perovskite oxide catalysts with moderate contents of oxygen vacancies. A high oxygen vacancy content would weaken the electron holes and redox couples, leading to poor ORR activity. Furthermore, too many oxygen vacancies may result in structure collapse [28, 29, 30].



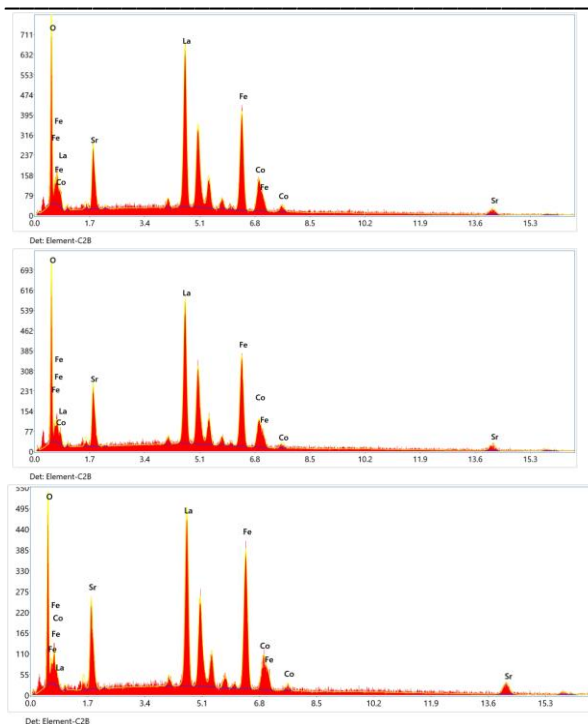


Fig.6. EDX spectra at a particular position of un-irradiated and radiated LSCF samples

Table.2. Quantitative of STEM analysis for oxygen concentration in all LSCF samples

Element	Un-irradiated LSCF	Radiated LSCF		
		20 KGy	250 KGy	500 KGy
O, Wt %	27	23	24	21
O, Atomic %	68	63	64	59

Conductivity study

The perovskite LSCF is a mixed ionic and electronic conductor [31, 32] due to presence of holes and oxygen vacancies. The ionic conductivity is about two orders of magnitude lower than the electronic conductivity, so it is assumed that measured value of conductivity is mainly due to electronic conductivity. Electrical conductivity measurements of un-irradiated and irradiated samples of LSCF were carried out using four-probe method from room temperature up to 500°C [33]. These results of electrical measurements are summarize in Fig.7 and table 3. These measurements can be taken into account as check points of the properties of synthesized perovskite material to be applied into cathode of solid oxide fuel cell. Fig.7 shows the DC conductivity studies of all the samples from room temperature to 500°C. The DC conductivity (σ) of the samples is

studied as a function of temperature using Arrhenius equation

$$\sigma = \sigma_0 \exp(-E_a/KBT) \quad (1)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy for conduction which is dependent on temperature carrier concentration and KB is the Boltzmann constant. The activation energy (E_a) of all the samples are calculated from the plot of $\log \sigma dc$ versus $1000/T$ as in Fig.7. The activation energy (E_a) values of all the samples are tabulated in Table 2. It is observed from the figure that DC conductivity increases with increase in temperature which represents a semiconductor behavior.

Also, electrical conductivity decreased at high temperature due to loss of oxygen and formation of oxygen vacancies.

These positive results of maximum conductivity, porosity, surface area and formation of oxygen vacancies have a significant conclusion on the performance of LSCF cathode in SOFCs. Also there is no transition from semiconductor to metallic behavior over the temperature range used in our study. Activation energy of all the samples at high temperature region is calculated by linear fitting the data from $\log \sigma dc$ and $1000/T$ graph and are summarized in Table 2. According to table 2, The maximum conductivity values for all LSCF samples were higher than other studies [34,35]. Also It was found that the maximum conductivity increase and the activation energy decrease by increasing the radiation dose. This may be due to the decreasing of oxygen atomic percentage and consequently the increasing of oxygen vacancies as shown in EDX analysis Table [2]. This mean that the electrical conductivity was tuned as a function in preparation condition. Also it was observed that the oxygen vacancies play a major role in this tuning.

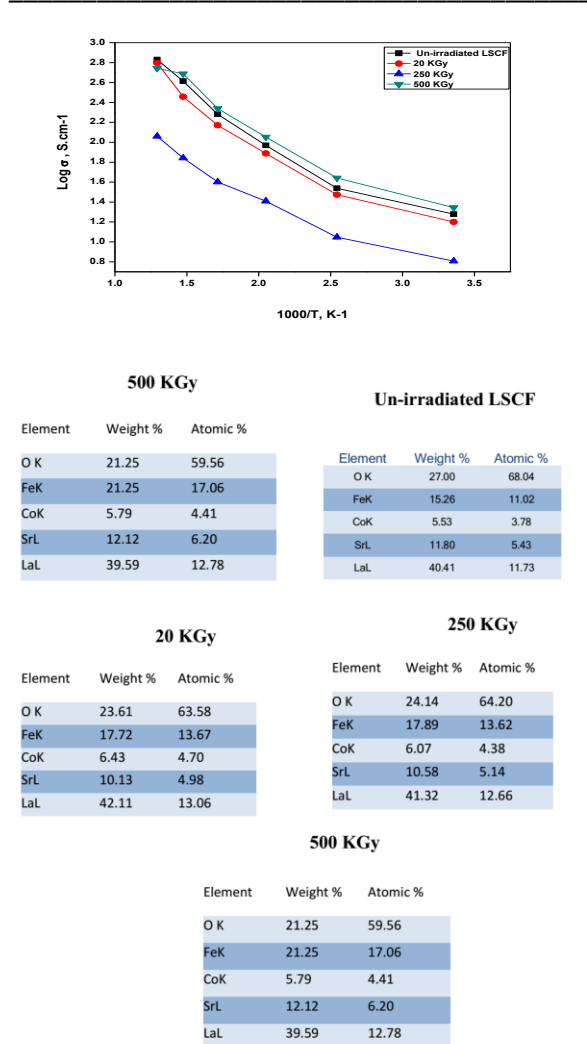


Fig 7. Electrical DC conductivity of un-irradiated and irradiated LSCF samples (20 kGy , 250 KGy and 500 KGy)

Table.3. Dc conductivity and calculated activation energy values

Sample	Dc electrical conductivity (σ) S/cm	Activation Energy (E_a), eV
Un irradiated LSCF	677	$2.045 * 10^{-4}$
20 KGy	627	$2.013 * 10^{-4}$
250 KGy	115	$1.698 * 10^{-4}$
500 KGy	553	$1.8836 * 10^{-4}$

Conclusions

This research work was designed to understand the influence of gamma irradiation on LSCF cathode material with absorb dose (20 kGy, 250 kGy and 500kGy) variation and finally confirmed about its

impact by studying some structural and physical properties.

A promising cathode material for (IT- SOFCs) LSCF was synthesized by sol gel and modified sol gel by gamma routes. we show that irradiation of materials is an innovative methodology due to the relative simplicity and favorable additive nature of radiation dose experiments which had strong influence on internal micro structure ,specific surface area and Dc electrical conductivity. Results showed that method of preparation affects microstructure of the LSCF samples. The XRD patterns of both routes showed a single-phase of LSCF perovskite material. It was found form BET and FESEM that LSCF synthesized by irradiation method showed phase perovskite product with more porous structure and higher surface area at 20 kGy. Also It was found that the dc electrical conductivity values were higher than other studies; which it is very important for performance of LSCF cathode in SOFC. The compositional characterization results showed that the irradiated samples contain more oxygen vacancies than did the un-irradiated sample and this has the effect on improving the cathode performance. It can be concluded from the obtained results that the effect of irradiation has a major role in inducing the oxygen vacancies. These oxygen vacancies in turn tuning the morphology, surface area and the dc electrical conductivity for optimum performance of the LSCF cathode in SOFC . It is worth noting that the radiation effect was not monotonic behavior. But it was found that the irradiated LSCF sample with 20 kGy ; which has higher porosity, high surface area, smaller particle size and relatively high electrical conductivity was more convenient for IT-SOFC cathode application than un-irradiated one.

Conflict of interest:

In behalf of the authors I confirm the Compliance with Ethical Standards, the work has been done without Funding from any external organization, and there is no Conflict of Interest with fully Ethical Conduct

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