Materials Innovations

HΣXA Publishers

Nanocomposites | Research Article | http://doi.org/10.54738/MI.2022.2501

High Performance of SDC Composite Electrolyte Using Natural Gas as a Fuel for Low Temperature SOFC

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OPEN ACCESS

Received: 14 April 2022
Accepted: 18 May 2022
Published: 28 May 2022

Citation: Yasmin N, Safdar M, Iftikhar A, Ahmad M, Mirza M (**2022**) High Performance of SDC Composite Electrolyte Using Natural Gas as a Fuel for Low Temperature SOFC. *Materials Innovations* 2 (5), 132-138.

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Published By Hexa Publishers

ISSN
Electronic: 2790-1963

In this work, nanocomposite of Lithium and Samarium doped Ceria (Li-SDC) is synthesized by means of polyol process to obtain dense electrolyte material for low temperature Solid Oxide Fuel Cell (SOFCs) without any chelating agent. The crystalline structure of nanocomposite material is examined by X-ray diffraction (XRD). The fuel cell performance is obtained at temperature range 500-550 °C. The conductivity of material was measured by 4-probe method. The prepared material morphology and microstructure analysis was studied by scanning electron microscope (SEM) images. The best results are obtained with sample which was prepared by polyol process gives 0.016 S/cm conductivity and it shows maximum power density of 0.2 W/cm^2 at 500 °C and 0.3 W/cm^2 at 550 °C respectively using natural gas as fuel. These results prevailed that the prepared electrolyte using polyol is best for low temperature SOFC. It is also noticed that as electrolyte ionic conductivity increases the performance of cell is also enhanced.

Keywords: Nanocomposite, LiSDC, Conductivity, SOFC, Electrolyte

INTRODUCTION

At present, electrical power is considered as important part of our lives. Sustainable energy, steadfast and environmental friendly power resources are the backbone to enhance the standard of current lifestyle. The reduction in the fossil fuels attracts the attention of researchers towards alternative energy resources. Fuel cells, for example, have been around for more than 1.5 centuries and provide an endless source of energy that is both environmental friendly and always available. Fuel cells have become increasingly popular over the last decade, with the goal of laying the ground work for future innovation, as they provide high efficiencies and are highly adaptable in power applications.The bulk of energy organizations are focusing on this invention, and there is currently a thriving commercial company exchanging fuel cells. Power corporations' residence relies upon on the two variables, cost and the long closing lifestyles cycle of fuel cell. Due to electrochemical reactions, chemical energy is converted into electrical energy using a tool known as a fuel cell with the help of an oxidizing agent. They are extremely efficient because they are not subject to the Carnot limiting criteria. Most crucially, when it comes to internal combustion engines, dangerous pollutants such as nitrogen oxides and sulphur dioxide are no longer produced[1–3].

Among all fuel cells kinds, SOFCs are most tempting because of its higher performance and low pollution. Numerous researchers concentrated on SOFCs toattain the exceptional performance by thecell. They mixed a variety of combos of SOFCs, in order to achieve extremely high energy densities and exceptional conductivity at low temperature. By improving reaction at electrodes and enhancing ionic conductivity of electrolyte many researchers are trying to lower the working temperature of SOFCs[4,5]. This can be obtained by using such fuels (like CH_4, H_2, H_2S, C_3H_8 etc.) that not only improve life time but also reduced the cost of cell. Gadolinium doped Ceria (GDC), Yttria stabilized Zirconia (YSZ), Scandia stabilized Zirconia (ScSZ), Yttria doped-Ceria (YDC), Samarium doped Ceria (SDC), and many other ceria composites are utilized to enhance electrolytes ionic conductivity. At low temperatures i.e. less than 700 ^{O}C as compared to zirconia based electrolytes the ionic conductivity of electrolytes which based on ceria are better. Ionic conductivity depends on composition and crystalline quality. However, better ionic conductivity can be got through grain boundaries and crystalline size[6,7]. Both ionic and electronic conduction is established by pure CeO_2 fluorite type structure but on the other hand has poor oxygen ion conduction. With the help of rare earth elements like Gd^{+3} and Sm^{+3} the oxygen ion conductivity might be improved. These low valence dopant cations not only enhance oxygen ion conduction but also increase ionic and electronic conductivities[6,8].

At low temperatures ranging from 450-700 ^{O}C doped electrolytes of ceria base demonstrate better efficiency but due to mixed conduction their efficiencies remain lower. As electrolytes ionic conductivity increased the efficiency of cell may also be increased. Different researchers used different approaches to enhance the ionic conduction. Alkaline salts in doped ceria create a new phase called the second phase with matrix phase ceria doped. For SOFCs natural gas is getting a valuable attention. For generation of energy hydrocarbon direct use results into deposition of higher temperature[6–8].

In present work Lithium ceria composite as electrolyte are synthesized while its structure, cell performance and thermal stability are investigated by using natural gas as fuel.

EXPERIMENTAL SETUP

Lithium Samarium doped Ceria (Li-SDC) as electrolyte for SOFC prepared by using polyol process.

With the use of a measuring balance, I measured 13.02 g of $Ce(NO_3)_2.6H_2O$, 1.229 g of $Li(CO_3)$, and 4.44 g of $Sm(NO_3)_3.6H_2O$. As a reducing agent, 100mL tetra-ethylene glycol dimethyl ether was placed in a beaker and heated and stirred continuously using a magnetic stirrer. The temperature of the magnetic stirrer was set at 200 ^{O}C. After 5 minutes, add $Ce(NO_3)$ to the tetra ethylene glycol dimethyl ether and wait 2–5 minutes. Then, in the aforesaid solution, add samarium nitrate and stirred for 30 minutes while heating. After 30 minutes of samarium nitrate addition, had added lithium carbonate to the reducing reagent and stir constantly for another 30 minutes while heating on the magnetic stirrer at 200 ^{O}C. The solution changed the color during this procedure in the following pattern

White → yellow → dark brown

Solution is cooled down at room temperature. Centrifugation is utilized to separate the solid particles from the solution. The de-ionized water or ethanol was used in filtration process to wash the remained solid solution in centrifugation. When filtration process was completed the remained solids were put in the pettry dish and put the pettry dish in‘ oven at 200 ^{O}C for drying the remained solids solution. Then crushed this attained dry powder and put it in crucible and covered the crucible with lid and kept in furnace for calcinations in stepwise one hour at each temperature 300 ^{O}C, 500 ^{O}C, 750 ^{O}C, then placed used 4 hour at 850 ^{O}C respectively. The final obtained powder after calcination; it was grounded for further characterization. Crushed the calcinated specimen and made two pallets via applying pressure on it. **Figure 1** illustrates the experimental detail.

- One was complete fuel cell with anode, electrolyte and cathode. The composite anode Ni/Zn oxide material and cathode was BSCF (barium strontium cobalt iron oxide) conventional material were used for cell preparation and testing.
- Other was pure electrolyte pellet (Li-SDC) for conductivity measurements

Fuel cell pellet has 0.64 cm^2 active area.

Pellet thickness is 1mm and diameter 13 mm.

RESULTS AND DISCUSSION

XRD analysis

Figure 2(a) reveals XRD pattern of Li-Samarium doped Ceria (Li-SDC). All peaks in the XRD pattern reveals that there is no evidence of SmO due to their proper doping in ceria. The crystallite sizes (D) were determinedthrough the Scherrer’s formula given below:

$$D = \ K\lambda/\beta cos\theta$$

Where θ is the angle between X-ray beam and sample.

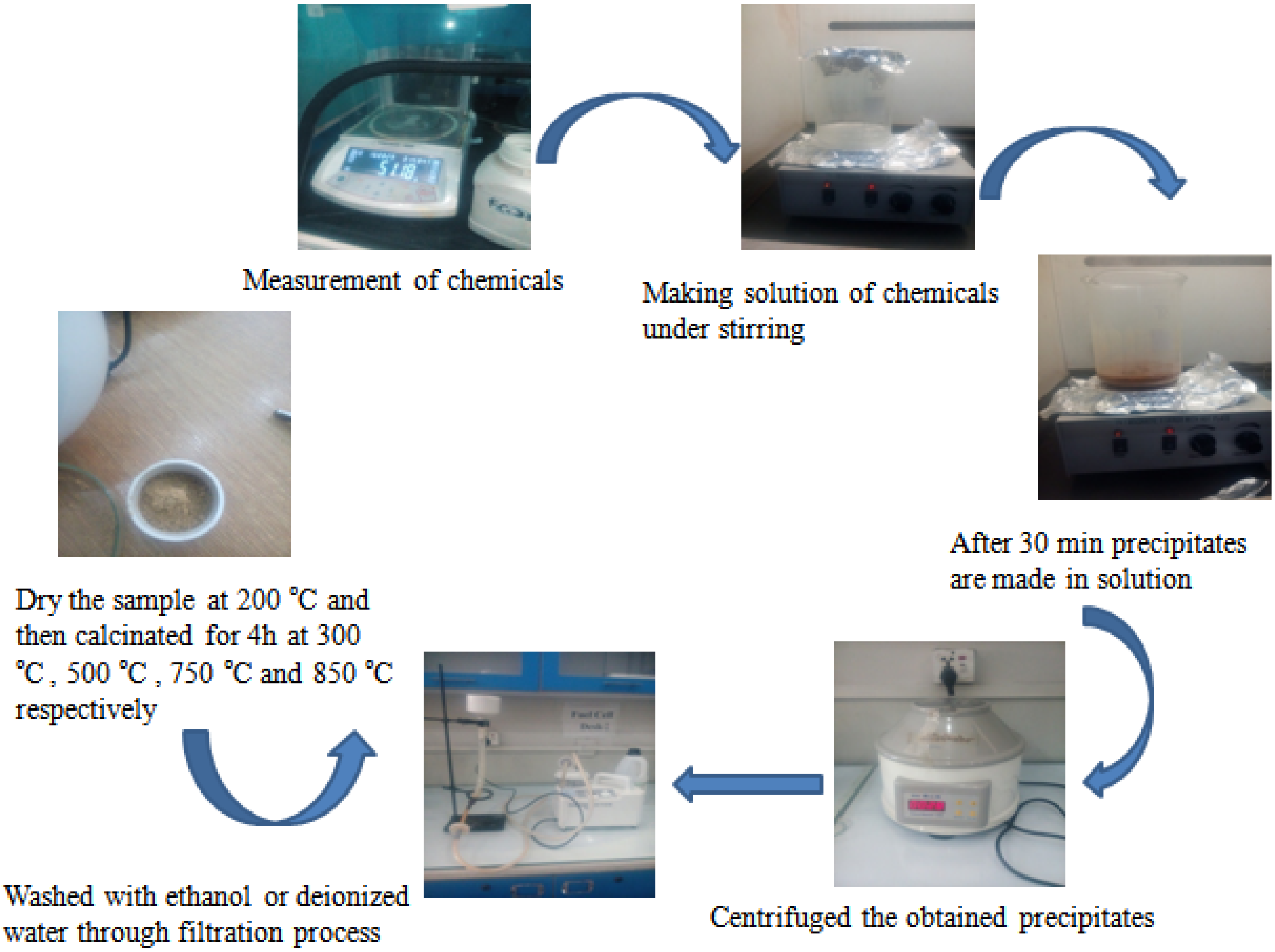

Figure 1. Schematic illustration of experimental details.

$\lambda \rightarrow$ X-ray wavelength

$\beta \rightarrow$ fullwidth at half maxima (FWHM)

D $\rightarrow$ crystallite size

Nano particle assemblies allow three dimensional confinements that lead synthesis of polygonal nano crystal of (Li-SDC) with size 200-500 nm. In this XRD pattern, high temperature treatment during fabrication caused high diffraction intensities[9], and better crystalline are formed at higher sintering temperature[10].

SEM analysis

Figure 2(b) reveals SEM analysis of prepared samples. SEM showed high density, with well-defined grains shape and homogeneous surface. To evade stresses in the specimen the process sintering temperatures was determined warily and clogged the heating when the grains started to demonstrate slip bands. At 800 ^{O}C dense microstructures has been showed by Li doped SDC. By increasing sintering temperatures and Li doping may reinforce grains growth. The observed average-grain size was found 200-500 nm. Because of nano particles the conductivity of our composite is high. The size of grain boundaries of these nanoparticles are large which is also favorable for increased conductivity of composites[11] as by this contact resistance reduces which provide a path way for ions to pass through interfaces of particles more easily[12,13].

The Li doped SDC showed dense microstructures at 800 ^{O}C because presence of Li_2O encourages densification. At 247.4 ^{O}C lithium nitrate starts melting while at 485 ^{O}C it starts decomposing[14]. Lithium oxide is formed and also possibly on the surface of Li-SDC grain, liquid of Ce-Sm-Li-O formed during sintering[15]. At the grain surface of SDC it seems that Li_2O adsorbed and formed thick layer around SDC. It may make sense that during sintering it will help SDC to transport and rearrange by enhancing the diffusion rate[16], and then densification was increased and hence required sintering energy was reduced. Li_2O lowered the sintering temperature of SDC by changing core struc-

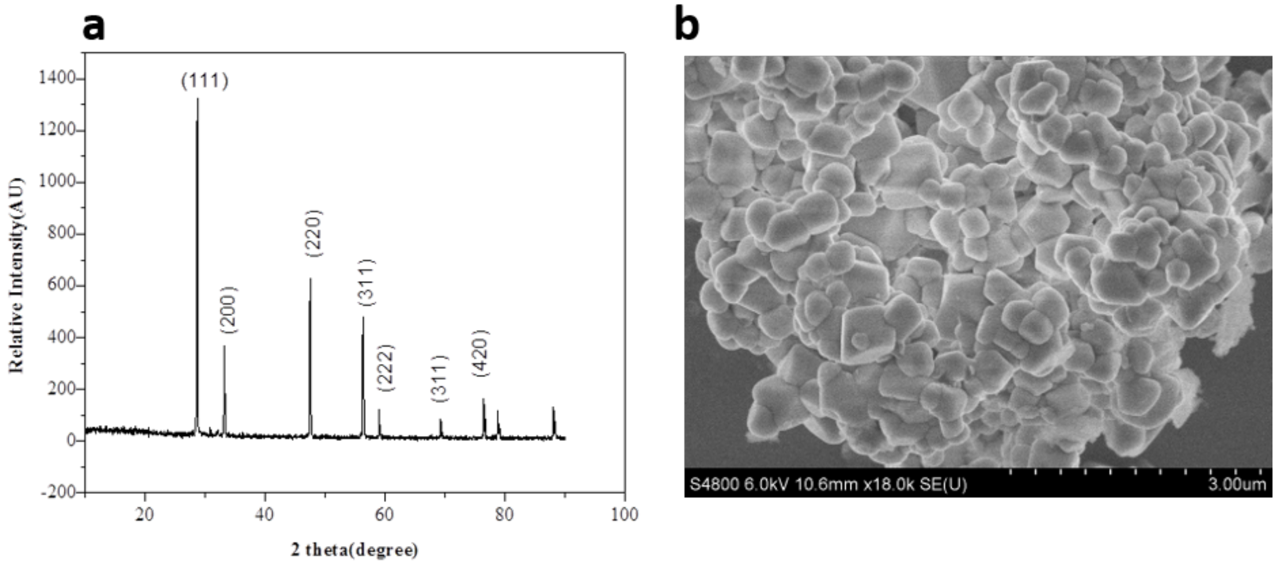

Figure 2. SEM images of Lithium and Samarium doped Ceria (Li-SDC).

ture of grain boundary. Therefore, at grain boundary of SDC more Li_2O will stay[17].

IV/IP curves

The polarization curve shows the fuel cell's voltage output for a particular current density loading.

Fuel cell polarization curve has three main regions:

- The activation polarization causes the cell potential to decline at low power densities.
- Because of ohmic losses, the cell potential drops linearly with current at moderate current densities.
- Due to more distinct concentration polarization, the cell potential drop deviates from the linear relationship with current density at high current densities.

Schematic measuring setup of IV/IP curve is shown in Figure 3. When a fuel cell's current (load) is changed, the fuel cell's heat and water balance shifts, and it can take some time to find a new equilibrium point. During testing, the fuel cell should be given a set amount of time to attain its new equilibrium. Whether the fuel cell load has been increased or decreased affects the formation of an equilibrium phase. The load can be designed to rise or decrease by a specified step-size, or the load can be randomly selected to collect relevant test data from the fuel cell in a various ways. The most common way is to gradually raise the load. Multiple current or voltage points can be used to collect data. Beginning with open-circuit voltage is a common way for taking measurements. Reliable voltage/current curves necessitate a stable environment in which pressure, humidity, flow rates and temperature remain constant throughout the test. The voltage/current characteristics may alter if the conditions change. In our case polarization curve is shown in Figure 4(a).

Fuel cell performance with the synthesized electrolyte of Li-SDC has been inspected in 500 to 550 ^{O}C temperature range. During this process natural gas is utilized as fuel in this cell and the supply rate is 100 mlmin^{-1}at 1 atm pressure at anode side and air is provided towards cathode side by using air pump. Figure 4(a) shows IV/IP curves provided maximum power density of 0.2 W/cm^2 at 500 ^{O}C and 0.3 W/cm^2 at 550 ^{O}C respectively[18] . The fuel cell performance shows that the prepared electrolyte has very good compatibility with the electrodes used in the cell. The IV curve showed that there is very small polarization losses at low temperature as compare to the high temperature reported work. The maximum obtained open circuit voltage (OCV) was 0.9 V at 550 ^{O}C. It is further noticed that the small drop of OCV and power density is due to the dense composite electrolyte which was obtained due to this new polyol preparation method.

Arrhenius plot

The Li-SDC ionic conductivity was tested with the help of four probe dc technique of with 13 mm pellet which was pressed under pressure of 300 MP with hydraulic press. For good conductivitysilver paste was utilized to paintthe synthesized pellets. The obtained results were plotted through origin pro 8.0 software. The conductivity is calculated by given formula:

$$\sigma = L/RA$$

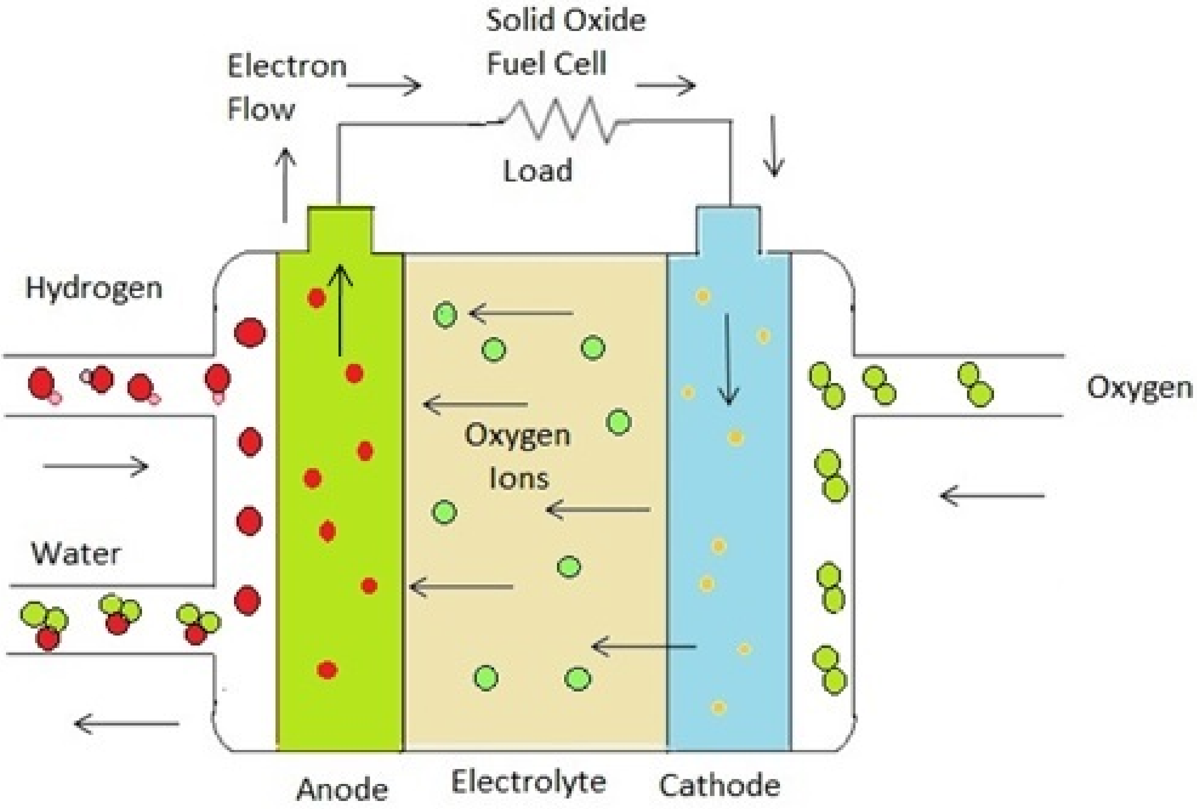

Figure 3. Schematic measuring setup of IV/IP curves.

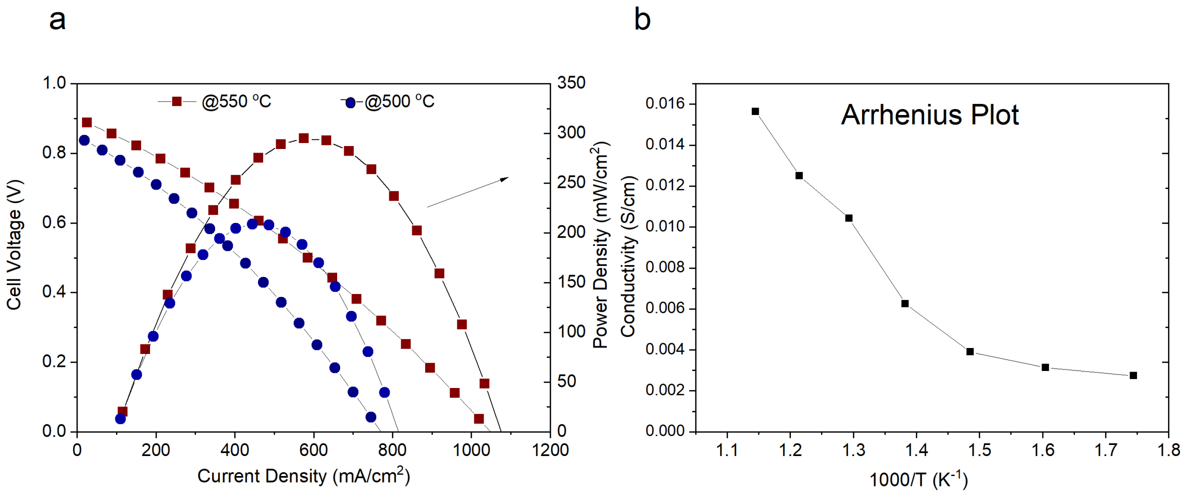

Figure 4. (a) The fuel cell performance Lithium and Samarium doped Ceria (Li-SDC) With Natural Gas as fuel. (b) Conductivity of prepared electrolyte (Li-SDC).

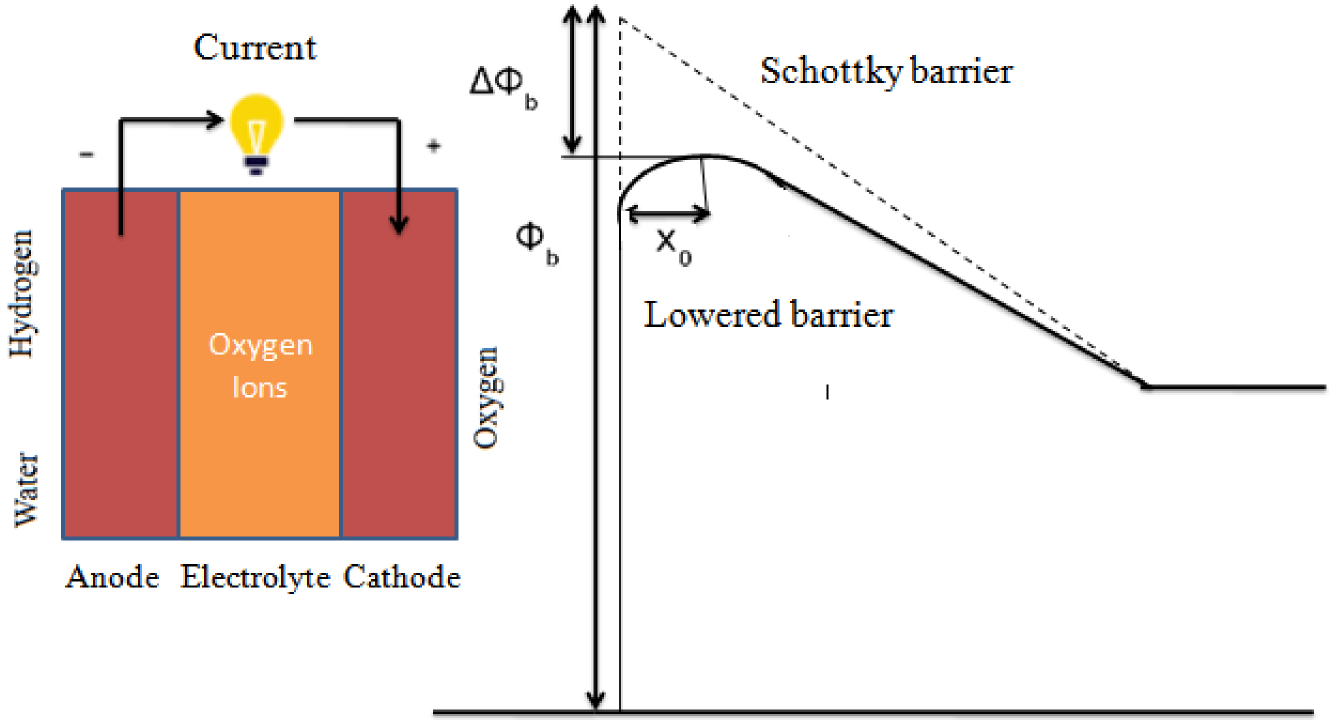

Figure 5. Mechanism of lowering Schottky barrier height in SOFC.

Where, σ is ionic conductivity,A is active surface area of pallet, R is internal resistance and L is thickness of pallet. Plotted Arrhenius graph showed conductivity of 0.01 S/cm[19] as shown in Figure 4(b). As reported by other researchers, due to low Ohmic losses, the performance of SDC based SOFCs is superior as compared to others[20–22] . According to GuO and Waser[23], the decrease of Schottky barrier height ($\Delta\Phi$) is due to Li^+enrichment, while the mechanism of lowering Schottky barrier height in SOFC is shown in Figure 5. Thus in space charge layers, it reduces the depletion of oxygen vacancies. Due to presence of Li_2O with SDC it results in enhancement of conductivity of grain boundaries[17].

CONCLUSIONS

Nanocomposites Lithium Samarium doped Ceria (Li-SDC) was synthesized using a polyol and developed as electrolyte for SOFCs. In present work IV/IP curves give maximum power density of 0.3 W/cm^2 at 550 ^{O}C. The maximum conductivity of 0.016 S/cm was achieved which is sufficient for any good fuel cell. The improved performance of fuel cell, conductivity and stability of the cell revealed that the prepared electrolyte is very dense and up to the mark for low temperature SOFC (solid oxide fuel cell). Hence, Li-SDC can be used as electrolyte for low temperature SOFCs by using natural gas as a fuel. Also, during sintering, at boundaries Lithium stays as liquid, which helps to enhance the conductivity of grain boundaries and also activate the surface of SDC at low temperature. In grain boundary of space charge layer, the depletion of oxygen vacancies depleted which results in enrichment of concentration of oxygen vacancy in grain boundary which leads to increase in conductivity of SDC.

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