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# **Barium Doped Ceria Based Material and its Electrochemical and Photocatalytic Properties at Low Temperatures**

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Energy demand and environmental degradation became the cause of alarming situation for the entire world. Therefore, switching from conventional to non-conventional or renewable energy sources is urgently required. In the era of renewable energy resources, solid oxide fuel cells (SOFCs) are more fascinating owing to their multiple properties and functionalities. The electrolytes are considered as the key component in fabrication of SOFCs. To overcome SOFC-related problems such as high operating temperatures, it is difficult to develop appropriate materials for the electrolyte. Herein, we developed novel nanocomposites as barium doped ceria (BDC) electrolyte material coated with alkali carbonates via cost effective co-precipitation and sol-gel routes. X-ray diffraction (XRD), scanning electron microscopy, and other techniques were used to examine the structural, morphological, elemental, and optical characteristics of synthesized electrolyte materials (SEM), energy dispersive spectroscopy (EDS), and photoluminescence spectroscopy (PL). The DC conductivity and cell performance measurements were recorded using four-probe technique and fuel cell testing unit. Results depicted that the average crystallite size lies in the range of 23-29 nm. The electrolyte material prepared by coprecipitation has dense structure; particles are well placed with each other and have shown maximum ionic conductivity of 0.2 Scm<sup> $^{-1}$ </sup> at 550 °C. The highest power density of 383 mWcm<sup> $^{-2}$ </sup> with open circuit voltage of 0.89 V is obtained at 550 °C with BDC electrolyte prepared by co-precipitation method. The

result showed that prepared electrolyte materials can be considered as the best alternative for SOFC applications. Photocatalytic degradation of Congo Red dye has been checked using BDC material prepared by co-precipitation method showing 77.89 % degradation efficiency, while BDC material prepared via sol gel method showed degradation efficiency of 68.42%. Degradation of Rocephin antibiotic has also been calculated as 54.27% by BDC from co-precipitation method, whereas BDC prepared by sol gel method depicted the percent efficiency of 48.24% respectively. Thus the comparative efficiency of prepared BDC materials provides a better choice because for fuel cell application, it is used as an electrolyte and photocatalyst for degradation of dyes and antibiotics in near future.

Keywords: Energy conversion; higher power density; ionic conductor; organic dyes; photocatalysis.

# **1. INTRODUCTION**

Worldwide energy demand is expanding, leading to the highest consumption of fossil fuels and extreme natural destruction [1]. By using proficient and renewable energy resources, these encountered issues can be resolved [2]. The energy conversion devices like solar cells, fuel cells and batteries, all are of key importance especially fuel cell (FC) might be considered the best option, as it converts fuel's chemical energy into electrical energy reliably with steam as only byproduct. Fuel cells and solar cells are considered proficient, economical, and secure alternative energy resources for portable and automotive applications [3-6]. Because of their high efficiency, reliability, fuel flexibility, ease of fabrication, environmentally friendly nature, and high potential for power generation, solid oxide fuel cells (SOFCs) are more promising among different kinds of fuel cells [7]. SOFCs utilize solid electrolyte which possesses excellent potential for oxide ions produced at cathode, and impermeable for electrons formed at porous anode [8-11].

In SOFCs materials, yttria-stabilized zirconia (YSZ) electrolyte materials have been used traditionally with working temperature ranging from 800 to 1000 °C. However, YSZ electrolyte materials cannot conduct enough oxygen ions at low temperature and reduces cell performance [12-13]. A crucial hindrance in SOFC advancement that limits its commercialization is the thermal mismatch of conventional electrolyte materials (operatable at high temperatures) with novel electrodes (that operates between 450 °C to 600 °C). The low working temperature can reduce the cell materials degradation and increases the choice of appropriate material selection. It also enhances the durability of cell and reduces the price of system [14]. For its industrialized application, Innovative materials with excellent mechanical and chemical stability, compatibility, and increased conductivity must be considered. The reduction of price rates, faster start-up and durability of LTSOFCs enable them more suitable for many applications including uninterruptible power supplies (UPS), auxiliary power units (APU), and remote power generation [15].

Cerium oxide (ceria, CeO<sub>2</sub>) is used in a wide range of applications such as gas sensors, memory devices, catalysts, energy conversion, and energy-storing systems [15]. In fuel cells, Ce (M)  $O_{2-\delta}$  (M: rare-earth or alkaline-earth cations) is of substantial attention for possible use due of its increased ionic conductivity and morphological variations. Ceria is therefore specifically investigated as an electrolyte material for SOFCs [16].

As a fuel cell electrolyte, CeO<sub>2</sub> has gained a lot of attention in recent years because of its ability to store the oxygen and release it via simple Ce<sup>4+</sup>/Ce<sup>3+</sup> redox cycles [17-18]. At high temperature, pure CeO<sub>2</sub> can easily sintered and hence have low thermal stability resulting a rapid decrease in its catalytic activity and oxygen storage/release capacity [19-20]. Moreover pure CeO<sub>2</sub>, an insulator has very low ionic conductivity ( $10^{-5}$  Scm<sup>-1</sup>) [21]. To overcome it, one method to do is doping with lower valence metal cations, specifically for some trivalent rare earth cations. Because of the charge neutrality and non-stoichiometry compensation, [22] rare earth cation doping can generate ceria lattice disorder and stress, which may make it easier for oxygen to move from the ceria lattice to its surface and lower the activation energy of formation of oxygen vacancy Hence, by rare earth doping, oxygen vacancy concentration is increased that lead to rise in oxygen ionic conductivity [23].

The ceria oxide based nanocomposite electrolyte materials have been considered as an important source of discussing conductivity because of their efficient ionic conduction behavior [24]. Doped ceria's surprising oxide ion conductivity makes it feasible for SOFCs to operate at lower operating temperatures, hence diminishing many technological issues [25]. The doping of cerium oxide with aliovalent cations creates oxygen vacancies for successful charge generation, oxide ions movement, and establishment of higher conductivity compared to pure cerium oxide. Many distinctive rare earth metals were already used for cerium oxide doping including Nd, Sm, Er, La and Pr, Y and Gd [26].

Recently, ceria-based nanocomposite electrolytes as sodium and potassium carbonated calcium doped ceria (NK-CDC) and gadolinium doped ceria (GDC) were introduced which showed high ionic conductivity in the range of 400-600 °C [27-29]. In another study, gallium doped ceria showed significant improvement on ceria reduction and altering acid–base and redox features of fluorite structured ceria electrolyte. The redox features were dramatically improved in gallium doped ceria materials as compare to pure ceria [30].

It was reported by Bi and his co-workers that use of barium-based electrolyte provides favorable circumstances for increased proton conductivity and consequently higher effectiveness for solid oxide fuel cell, implementing the Efros-Shklovskii hopping/ conduction mechanism among nearby oxide ions [31]. In another research endeavor Bi and coworkers using BZY Cells with  $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$  nanoparticles at 600 °C obtained maximum power density value of 602 mWcm<sup>-2</sup> [32].

Some reports have shown that the doping of barium can increase the ionic conduction of ceria electrolytes and decrease the working temperature due to its protonic conduction in SOFCs electrolytes [33]. F. Altaf and her colleagues reported Ba/Ga supported ceria electrolyte material synthesized by coprecipitation technique for LTSOFC. They obtained excellent values of current density (893 mAcm<sup>-2</sup>) and power density (375 mWcm<sup>-2</sup>) at 650 °C [34]. Similarly, the development of barium doped ceria with higher power density; good working efficiency has gained much interest in practical applications [35-37].

There are various kinds of fabricating techniques that have been used for the preparation of metal oxide nanocomposite electrolytes including microwave, ultra-sonication, ball milling, sol-gel, mechanical alloying, and co-precipitation [38]. Among above all mentioned techniques, Co-precipitation is a friendly process that leads to a quick and homogenous reaction, making it more useful for the production of composite electrolyte. For creating homogeneous and extremely pure sample with small particle size in shorter time with energy efficient ways, this technique is more useful [39-40].

Considering applications of ceria based materials in photocatalytic degradation of organic dyes and certain drugs, fruitful results have been recorded in this field. Because of better separation of h+/epairs, the increased photocatalytic activity was observed by CeO<sub>2</sub> doping with metals. Charge carrier localization is facilitated by metal dopants [41]. In order to form alkaline metal ion-doped cerium oxide nanostructures, the hydrothermal approach was used. Degradation of Methylene Blue dye was two times higher indicates increased CeO<sub>2</sub> photocatalytic activity due to the Mg, Ba, Ca and Sr were applied as dopants [42]. Similar studies were carried out when nanoparticles of Ag, Bi, Cd, and Pb of CeO<sub>2</sub>. CeO<sub>2</sub>/Ag had the best photocatalytic activity among other doped ceria, because to its high electrical conductivity, wide surface area, superior stability, and band gap decrease to 1.86 eV [43].

In the current study, the barium doped ceria prepared *via* co-precipitation and sol-gel techniques were investigated systematically. The crystallinity was observed using X-rays diffraction. The surface morphology with elemental composition was determined *via* SEM and EDS and electrochemical measurements were carried out to check the conduction and performance for LTSOFC. Moreover, photocatalytic degradation of Congo red dye and Rocephin antibiotic were calculated and compared to show the versatility of synthesized materials.

# **2. EXPERIMENTAL**

# 2.1. Materials Used

All the chemicals used were of analytical grade and no further purification was done before using. The chemicals being used are listed as; Cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O), Barium nitrate (Ba(NO<sub>3</sub>)<sub>2</sub>, Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), Sodium Hydroxide (NaOH), Citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>), Polyethylene glycol (PEG), Silver nitrate (AgNO<sub>3</sub>), Ethylene diamine tetra acetic acid (EDTA), 2-Propanol, Vitamin C (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>), Distilled and deionized water.

# 2.2. Synthesis of Barium Doped Ceria (BDC)

The barium doped ceria,  $Ba_{0.2}Ce_{0.8}O_{1.9}$  (BDC) electrolyte materials were synthesized *via* coprecipitation and sol-gel method followed by sintering. The first sample of BDC electrolyte material was synthesized by using the co-precipitation method with a weight ratio of  $Ce^{+3}$ :  $Ba^{+2} = 4:1$ . Initially, cerium nitrate hexahydrate ( $Ce(NO_3)_{3.6}H_2O$ ), and barium nitrate ( $Ba(NO_3)_2$  were dissolved in 500 ml deionized water and stirred with 150 rpm for 1 hour at 100 °C. In next step, 20 wt. % solution of precipitating agent sodium carbonate ( $Na_2CO_3$ ) was separately prepared in 100 ml deionized water and was stirred for 20 minutes with 150 rpm at 100 °C. The prepared hot solution of the precipitating agent was poured drop wise into BDC solution. The mixture was again stirred for half an hour. Precipitates formed were filtered using the dry suction pump and washed several times to get the final product, followed by oven drying oven at 200 °C for three hours. Finally, for four hours the powder was sintered in a muffle furnace at 800 °C and using mortar & pestle it was ground to get the desired powdered material.

The second sample of BDC was prepared *via* sol-gel route. The precursors, cerium nitrate hexahydrate ( $Ce(NO_3)_3.6H_2O$ ), and barium carbonate (BaCO<sub>3</sub>) were used as starting materials. The stoichiometric amounts of cerium nitrate and barium carbonate were dissolved in 100 ml deionized water

with a weight ratio of  $Ce^{+3}$ :  $Ba^{+2} = 4:1$  and stirred with 150 rpm for 1 hour at 100 °C. In next step, 20 ml of NaOH solution was poured drop wise in BDC solution followed by the addition of 20 wt. % of citric acid, and polyethylene glycol (PEG) solution as chelating agents. The mixing was carried out by continuous stirring at 100 °C till gel formation. After that, at 200 °C gel was dried in oven for three hours. The obtained product was sintered at 800 °C for four hours in digital Muffle Furnace. Then sintered sample was ground using mortar and pestle to get final product.



Figure 1. Flow sheet diagram for the synthesis of Barium dopped Ceria material.

# 2.3. Conductivity Measurement

In order to measure the ionic conductivity, prepared nanocomposite BDC powder was placed into stainless steel dye to make the pellets and pressed under 300 MPa for one minute using a hydraulic press. The diameter of the dye was 13 mm and thickness of pellet was controlled at 1.2 mm. The prepared pellets were placed into a ceramic boat and fired for one hour at 600 °C. For better current collection, the silver mesh was adjusted on both sides. Further pellet was adjusted in four probe dye and data potential, current and resistance was recorded to calculate the ionic conduction under air and hydrogen atmosphere in the range of 250-550 °C with SMU (Keithley instrument Taiwan).

# 2.4. Fuel cell fabrication

Three layered symmetric fuel cell based on newly prepared BDC electrolyte sandwiched between symmetrical electrodes LiNiCuZn-O (LNCZ) [44]. Nickel-foam in circular form was cut and implanted on the anode side of the pellet to provide sufficient porosity for hydrogen fuel diffusion. After that, at 600 °C fabricated cell was heated for one hour and remaining side was painted with silver paste. Fuel supplied rate was controlled at 100 ml/min in case of electrolyte material prepared by co-precipitation and 160 ml/min for the material proposed by sol-gel after observing maximum open circuit voltage at 1 atm pressure. Four probe stainless steel dye was used to adjust the pellet/cell during conductivity measurements in the digital furnace.

# 2.5. Characterizations

The phase pattern was analyzed through X-ray diffraction (XRD) by PANalytical X'Pert Pro MPD Netherland, with Cu Kα radiation having scanning rate 0.005, 30 mA and 35 kV at room temperature. To measure the crystallite size, Scherrer's equation was applied.. Further Williamson Hall formula was applied to calculate the lattice strain produced in crystal structure due to barium doping. Scanning electron microscopy (SEM) VEGA TESCAN was used to observe the particle size, density and surface morphology. Optical properties were studied using photoluminescence spectroscopy via confocal Microscope-Renishaw (UK). The conductivities were measured using DC four-probe Keithley instrument 2450 under air environment and hydrogen environment. Fuel cell performance was done using SM-102 fuel cell testing unit with eight variable resistors.

# **3. RESULTS AND DISCUSSION**

#### 3.1. X-Ray Diffraction Analysis

The X-ray patterns of the prepared electrolyte materials (BDC) have been shown in Figure 2 (a). The XRD patterns of both samples exhibited crystalline structure. All peaks were analyzed using X'Pert High Score software with crystallographic library ICSD. The electrolyte material prepared by coprecipitation method shows only single phase CeO<sub>2</sub> having cubic fluorite structure which matches with the JCPDS card number (00-001-0800). There is no peak that shows the presence of barium, which confirms that barium, is fully doped in CeO<sub>2</sub> structure during co-precipitation method. However, the second sample prepared by sol-gel has three additional peaks at the position of  $2\theta$ =38.20°, 46.79° and 64.56°, which match with barium cerium oxide Ba (CeO<sub>3</sub>) phase having orthorhombic structure with JCPDS card number (01-083-0532). It might be possible due to less quantity of doped barium in ceria- structure and remaining amount of barium appeared as second phase with ceria which reduces the vacancies for oxide ions [45]. The XRD results showed that the BDC sample prepared by co- precipitation method slightly diffracted toward higher diffraction angle with reduced crystal size. Lattice parameters of the cubic structure is (a= 5.4100 Å) with space group Fm-3m-225 and orthorhombic structure have (a= 8.7906 Å, b= 6.2517 Å, and c= 6.2271 Å) with space group Pmcn-62. The average crystallite size calculated was 28.6 nm in case of sol-gel prepared sample and 23.7 nm for the sample prepared by *via* 

co-precipitation. The major advantage obtained from cubic structure is the creation of vacancies for oxide ion movement [46]. The other benefit of barium doped ceria is reduction in current loss during cell performance because of partial change into oxidation state of ceria from tetravalent ( $Ce^{+4}$ ) to trivalent ( $Ce^{+3}$ ) [47]. The Lattice strain was calculated using Williamson-Hall formula and found to be 0.21%, and 0.13% for both materials prepared by sol-gel and co-precipitation respectively. The crystallite size of BDC electrolyte prepared by co-precipitation method decreased which indicates the rapid growth of crystal. The XRD patterns did not show any peak related to sodium carbonate due to its amorphous phase [48]. The presence of less crystallite size enhances the surface area which promotes higher ionic conduction.

# 3.2. SEM and EDS Analysis

Figure 2(b) and 2(c) shows the morphology of both prepared materials. In case of BDC electrolyte materials prepared by co-precipitation as in Figure 2(b), the particles are distributed in the range of 0.2-0.5  $\mu$ m and have dense structure with bunches of bright particles. The bright thin layer of alkali metal oxide (spread over the particles) can be clearly seen, which provides a better ionic pathway through interfacial surfaces. The prepared electrolyte material showed a porous silica beads like structure as shown in Figure 2 (b) which is softly embedded with each other. This morphological characteristic helps in the diffusion of oxide ion within the electrolyte layer. The SEM images exhibited that synthesized powder is consisted of the clustered phase. It can be anticipated that Na<sub>2</sub>O covers the BDC nanoparticles on rapid freezing after taking out from furnace in the form of thin bright layer and prevent the specie from agglomeration [49]. From Figure 2 (c) the particles are more uniform but have porosity which facilitates movement of oxide ion from the boundary of cathode to electrolyte. The EDS spectra of BDC materials are shown in Figure 2 (d), the results are well in agreements with the experimental stoichiometry indexes, where all the nominal composition of desired elements is confirmed.

# 3.3. Photo-luminescence analysis

In Figure 2 (e), the photoluminescence spectra of the BDC nanocomposites with excitation wavelength of 457 nm at room temperature. The emission spectrum exhibited by BDC near shorter wavelength (450-550 nm) in visible range with maximum emission of peak at 459 nm and 463 nm for BDC electrolyte prepared by co-precipitation and sol-gel respectively. PL band located at 425 nm to 525 nm attributed to trivalent cerium ion [50]. The intense peak at 459 nm describes the level of Ce<sup>+3</sup> ion falls into the crystal band gap. This band originates from the recombination process through cerium ion to other valence state Ce<sup>+3</sup> which effect the charge compensated when protons are incorporated with lattice [51]. BDC electrolyte prepared by sol-gel has second band located in the range of 550-600 nm which is attributed to BaO<sub>2</sub> [52]. Further reduced intensity of BDC prepared by sol-gel also decreases the conduction during cell performance.



**Figure 2.** (a) XRD of as-prepared samples,(b) SEM image of electrolyte material by co-precipitation method (c) SEM image of electrolyte material by sol-gel method, (d) EDS spectrum and (e) photoluminescence results with maximum emission peaks.

# 3.4. DC conductivity tests

The DC conductivities of both BDC electrolyte materials were measured by four probe method and results are presented in Figure 3. The pellets' active area was 1.13 cm<sup>2</sup>. The temperature dependent

ionic conductivity of prepared pellet was tested in the open-air environment and  $H_2$  environment as well. The findings suggested a semiconductor behavior and shown that conductivity increased with temperature. Variations in ionic conductivity are due to the release of lattice oxygen. The BDC electrolyte material prepared by co-precipitation showed the highest conductivity that is attributed to the ordered structure which facilitates the transportation of ions in the composite structure [24]. Conductivities were found in the temperature range of 250 °C to 550 °C. Initially, the conductivity increased gradually by increasing temperature with the interval of 50°C. After increasing temperature from 350°C to 550 °C, the conductivity values abruptly enhanced due to thermal expansion of material. In addition to this, the molten state of carbonate phase present in the electrolyte material/ composite is also considered as the reason for abrupt increase in conductivity. Another reason of sudden increase in conductivity is the migration of ions through carbonates which act as an interface for conducting carriers. The molten carbonate phase creates the path for fast conduction of oxygen ions and protons at relatively high temperatures [53]. However, upon further increase in temperature upto 550°C the slow enhancement of conductivity value was observed which signifies that polarization losses are produced in the material especially ohmic resistance. Maximum conductivity of 0.2 Scm<sup>-1</sup> is attained at 550°C under hydrogen environment for electrolyte prepared by co-precipitation. This value is greater than previously reported Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> samarium doped ceria. Ce<sub>0.8</sub>Ca<sub>0.2</sub>O<sub>1.9</sub> (CDC), Ce<sub>0.8</sub>Sm<sub>0.1</sub>Ln<sub>0.1</sub>O<sub>1.9</sub>, (SDC), SrCeO<sub>3</sub> strontium cerate, Ce<sub>0.8</sub>La<sub>0.2</sub>O<sub>1.9</sub> (LDC), Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub> and gadolinium doped ceria [54-58].

#### 3.5. Activation energy measurements

The next step was to check the activation energy (Ea) values of designed electrolyte materials were calculated using conductivity data by implying Arrhenius gas equation and as shown in Figure 3. In order to measure the slop; the linear fit technique was implemented. Further slop was multiplied by general gas constant that was taken in eV. The BDC electrolyte material prepared by co-precipitation showed minimum activation energy of 0.39 eV. This minimum activation energy (Ea) value indicates the better performance of cell in fast conduction of ions. These minimum activation energies values are considered as a good agreement with conductivity analysis.



Figure 3. (a) DC conductivity of the BDC samples, (b) Activation energy curves.

# 3.6. Working of fuel cell

The schematic representation of a typical SOFC working principle has been shown in figure 4, using an  $(O_2^{-})$  conducting electrolyte as a model. Cathode was provided with dry air and the molecular oxygen  $(O_2)$  flowing from the gas flow mix with electrons of the outer external circuit, as a result two oxygen ions are provided [10]. (Because of inert behavior of N<sub>2</sub> and other kind of such gases in the air media these are ignored.) The reaction occurred at cathode reaction is defined as follows:

 $1/2 \text{ } O_2 + 2e^{\text{-}} \rightarrow O_2^{\text{-}}$ 

Then the produced  $O_2^-$  ions move to the anode. Two electrons are released when the oxidation reaction take place at  $(H_2)$  fuel supplied and bond breakage occurred into two  $(H^+)$  ions. Generated electrons are transported towards external electric circuit ;when  $(H^+)$  ions combine with  $(O_2^-)$  ions [59]. At anode following reaction take place as:

 $H_2 + O^2 \rightarrow H_2O + 2e^-$ 

A full circuit in this SOFC device realizes mass transfer and electric current.

Overall electrochemical reaction is written as:

 $\mathrm{H_2} + 1/2 \ \mathrm{O_2} \rightarrow \mathrm{H_2O}$ 



Figure 4. Proposed Working Mechanism of Solid Oxide Fuel Cell. [11].

# 3.7. Fuel cell performance

The performance of prepared symmetric fuel cells was studied in the range of 450- 550 °C using air as an oxidant and  $(H_2)$  hydrogen as a fuel. Then the resultant current and open-circuit voltage (OCV) was measured using fuel cell testing instrument. By increasing the temperature, OCV decreased which shows the consistency of the law of thermodynamics and power density increased in case of BDC synthesized by co-precipitation displayed in Figure 5 (a).



**Figure 5.** I-V/I-P Fuel cell characteristics using Hydrogen (H<sub>2</sub>) acting as fuel at max of 550 °C using (a) Co-precipitation method and (b) Sol gel Method.

**Table 1.** Comparison of electrolyte materials synthesized using sol-gel and co-precipitation methods based on maximum values of ionic conduction in air and hydrogen environment, current density, open circuit voltage, power density and activation energy.

Electrolyte	σ (air)	σ (H <sub>2</sub> )	J	OCV at	Р	Ea
Materials	(Scm <sup>-1</sup> )	(Scm <sup>-1</sup> )	(mAcm <sup>-2</sup> )	550 °C (V)	(mWcm <sup>-2</sup> )	(eV)
BDC (co-	0.06	0.2	1290	0.89	383	0.39
precipitation)						
BDC (sol-	0.04	0.15	840	1.0	223	0.44
gel)						

BDC electrolyte materials synthesized through sol-gel technique, the OCV was also increased by increasing temperature. In addition to that, cell performance was too low at the fuel rate of 100 ml/min. However, upon gradual increasing fuel rate from 100 to 160 ml/min, the cell performance

became stable which shown in Figure 5(b). Excess fuel utilization may be due to porosity produced by overcrossing of air which occurred during synthesis. Capacity of the fuel cell material with fabricated composites, power density and current density values were calculated. Next the current density (J) of cell was plotted vs. voltage (V). Current densities (J) vs power density (P) graphs were plotted at 550°C temperature. Peak power density (P) was observed using H<sub>2</sub> (gas) noted was 383 mWcm<sup>-2</sup> at 550°C which is greater than previously reported (BaCe<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2.90</sub>) and (90 wt% Ce<sub>0.8</sub>Sm<sub>0.1</sub>Bi<sub>0.1</sub>O<sub>2-δ</sub>, 10 wt% BaCe<sub>0.8</sub>Sm<sub>0.1</sub>Bi<sub>0.1</sub>O<sub>3-δ</sub>, Bi-SDC-BCS) [60-61].

# 3.8. Photocatalytic degradation studies

In order to study the process of photocatalytic degradation of dyes, Congo Red (CR) dye has been used for this purpose. Percentage degradation (% D) of CR has been calculated by using barium dopped ceria (BDC) nanomaterials synthesized by sol gel methods and co-precipitation as a facile route separately. The standard formula being used for calculations of % Degradation is expressed in equation 1 as [62].



**Figure 6.** Removal of Congo Red via Photocatalytic degradation using (a) BDC material by sol-gel method and (b) BDC material by Co precipitation method.

Sr #	Initial Absorbance (A <sub>o</sub> )	Final Absorbance (A <sub>t</sub> )	Degradation (%)
1.	1.90	1.90	00
2.	1.90	1.61	15.26
3.	1.90	1.46	23.15
4.	1.90	1.34	29.47
5.	1.90	1.25	34.21
6.	1.90	1.13	40.52
7.	1.90	0.82	56.84
8.	1.90	0.71	62.63
9.	1.90	0.60	68.42

Sr #	Initial Absorbance (A <sub>0</sub> )	Final Absorbance (A <sub>t</sub> )	Degradation (%)
1.	1.90	1.90	00
2.	1.90	1.65	13.16
3.	1.90	1.37	27.89
4.	1.90	1.09	37.36
5.	1.90	0.93	51.05
6.	1.90	0.81	57.36
7.	1.90	0.70	63.15
8.	1.90	0.57	70.0
9.	1.90	0.42	77.89

Table 3. Degradation (%) of CR Dye using BDC material synthesized via Co-precipitation method.



**Figure 7.** Photocatalytic degradation of Rocephin Antibiotic using (a) BDC material by Co precipitation Method (b) BDC material by Sol Gel Method.

**Table 4.** Degradation (%) of Rocephin Antibiotic using BDC material by Co-precipitation method.

Sr #	Initial Absorbance A <sub>o</sub>	Final Absorbance At	%Degradation (%)
1.	1.99	1.99	00
2.	1.99	1.92	3.52
3.	1.99	1.83	8.04
4.	1.99	1.69	15.07
5.	1.99	1.51	24.12
6.	1.99	1.22	38.69
7.	1.99	0.91	54.27

Sr #	Initial Absorbance Ao	Final Absorbance At	Degradation (%)
1.	1.99	1.99	00
2.	1.99	1.93	3.01
3.	1.99	1.85	7.02
4.	1.99	1.73	13.06
5.	1.99	1.57	21.10
6.	1.99	1.32	33.66
7.	1.99	1.03	48.24

Table 5. Degradation (%) of Rocephin Antibiotic using BDC material by Sol Gel method.

# 3.9. Scavengers test

The radical trapping test had been performed to calculate the contribution of various radicals towards the degradation of Congo red dye and Rocephin antibiotic respectively as shown in figure 8. The trapping agents for the test were AgNO<sub>3</sub>, Vitamin C, 2-Propanol and EDTA were used for the electrons capturing, formation of superoxide radicals, hydroxides (OH<sup>-</sup>) and holes. For this purpose, trapping system of BDC materials was investigated and the results of 77.8 % to 13 % by AgNO<sub>3</sub> is the highest efficiency revealing that electrons generated during the photo-excitation which causes the degradation removal of CR and Rocephin antibiotic.



Figure 8. (a) Scavenging test for CR Dye (b). Scavenging test for Rocephin Antibiotic

# 3.10. Band Gap Calculations for BaO, CeO<sub>2</sub> and BDC material

The potential band edge of the semi-conducting material trigger the transfer of the photogenerated charge carrier ions [63]. As a result, the potential band edge value for barium oxide (BaO), cerium dioxide (CeO<sub>2</sub>) and BDC samples was calculated with the help following equations given as below:

$$E_{CB} = X - (E_{ef} + 0.5E_g)$$
 (2)  
 $E_{VB} = E_{CB} + E_g$  (3)

H-scale value of (~ 4.25 eV) was used in order to calculate the band gaps of (BaO), (CeO<sub>2</sub>) and BDC illustrated in figure 9. The reported band gap for BaO is 4.51 eV - 4.65 eV while its 4.44 eV for BaO has been measured in our work. Whereas, band gap for CeO<sub>2</sub> being reported so far report is 2.90 eV - 3.19 eV, while we have calculated 3.08 eV for CeO<sub>2</sub> [64-65]. The BDC material shows band gap of 3.54 eV, used for elucidating better photocatalytic performances for dyes as well as antibiotics.



**Figure 9.** UV-Visible absorption peaks with associated Tauc plots for calculating the band gaps of (a) BaO, (b) CeO<sub>2</sub> and (c) BDC.

# 3.11. Mechanism of Photocatalytic degradation by BDC material

Barium doped ceria (BDC) material when irradiated with visible light; both components of BDC, barium and cerium got excited resulting the production of photo electrons and holes in the conduction band (CB) and valence band (VB) for both materials.

The photogenerated  $e^-$  in the conduction band of CeO<sub>2</sub> can easily transfer to conduction band of BaO resulting O<sub>2</sub><sup>-</sup> (superoxides) which further reacts with dyes and other pollutants [66]. In the same

way, the photogenerated holes from valence band of BaO can move towards the VB of CeO<sub>2</sub> producing hydroxyl radicals (OH<sup>-</sup>) capable to react with dyes molecules respectively [50, 67].

Simplest reactions involved in the production of reactive species can be represented in equations as:

$$CeO_{2} + h\lambda \rightarrow CeO_{2} (e_{CB}^{-} + h_{VB}^{+}) \quad (4)$$
  

$$BaO + h\lambda \rightarrow BaO (e_{CB}^{-} + h_{VB}^{+}) \quad (5)$$
  

$$Ce^{4+} + e_{CB}^{-} \rightarrow Ce^{3+} \quad (6)$$
  

$$Ce^{3+} + O^{-} \rightarrow Ce^{4+} + O^{-} \quad (7)$$

$$H_2O + h_{\nu R}^{\dagger} \rightarrow OH^- + H^+$$
(8)

$$I_2 O + I_{VB} \rightarrow OII + II \qquad (8)$$

$$O_2^{-} + 4H^+ \to 20H^-$$
 (9)



Figure 10. Possible Mechanism of Photocatalytic degradation by BDC Material.

**Table 6.** Comparability effectiveness of BDC materials as photocatalyst for Organic dyes and Antibiotics under a variety of conditions.

Sr #	Photocatalyst	Quantity	Dye/ Antibiotic	Time (min)	% D	Reference
		used				
1.	Cr/CeO <sub>2</sub>	3%	Methylene Blue	100	41.4	[67]
2.	Fe-doped ZnO	5 mg	Congo Red	60	67.4	[68]
3.	Ba-doped g-C <sub>3</sub> N <sub>4</sub>	2%	Tetracycline	120	69.2	[69]
	nanocomposite					
4.	Nitrogen-doped	0.5 g/L	Sulfamethoxazole	150	96	[70]
	(N-doped) Ceria		(SMX)			
	nanocomposite					
5.	Barium Dopped	05 mg	Congo Red/	77.8 / 54.2	80/60	(Present work)
	Ceria (BDC)		Rocephin			

# **4. CONCLUSION**

The nanocomposite Barium doped ceria (BDC) electrolyte material has been successfully synthesized via co-precipitation and sol-gel methods. In both cases, the prepared materials showed crystalline behavior having cubic fluorite structure. However, the sample prepared by sol-gel showed cubic and orthorhombic structures as determined by XRD. The existence of dual phase for BDC electrolyte using sol-gel route shows that content of barium not fully doped with ceria at interstitial sights. The morphology of prepared BDC electrolyte by co-precipitation have a porous silica beads like structure which is softly embedded with each other, resulted in diffusion of oxide ion within the electrolyte layer. Alkali metal dopants melt during sintering and spread over the doping particle surface thus producing a second phase in the amorphous form which provides efficient channels for protons transportation. The elemental composition of BDC electrolyte was confirmed by EDS. The Photo Luminescence results of BDC electrolyte showed the recombination process of Ce<sup>+4</sup> ion into another valent state Ce<sup>+3</sup> which have greater influence for the transportation of protons through crystal lattice. The BDC prepared by co-precipitation has maximum protonic conduction of 0.2 Scm<sup>-1</sup> at 550 °C under hydrogen environment. Moreover, same material has low Activation energy (Ea) of (0.39 eV) which ensures that this material is well suitable as a potential material towards solid oxide fuel cells (SOFC). The BDC prepared by co-precipitation showed maximum power density measured was 383 mWcm<sup>-2</sup> at 550°C using air as an oxidant and hydrogen (H<sub>2</sub>) gas as a fuel. The above results showed that ionic conduction through barium doped ceria plays significant role in the conversion of fuel energy into electrical energy. The percentage degradation efficiency (%) of both materials of BDC for vitiation of Congo Red dye 77.89 % by co-precipitation method, while 68.42% by sol gel method. Degradation of Rocephin antibiotic has been calculated as 54.27% by co-precipitation method, whereas BDC prepared by sol gel method depicted 48.24% degradation efficiency respectively. Thus, the effort of synthesizing an appealing BDC material will be a prior choice to carry out more work in the relevant direction in near future.

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