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Research Article

Physico-chemical characterization of the effects of surfactant on samarium doped ceria ($Ce_{0.8}Sm_{0.2}O_2$) perovskite as electrolyte for low temperature SOFC application

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Abstract

Sol-gel technique was adapted to synthesize porous samarium doped ceria nanoparticles. The templating characteristics of Pluronic F-127 surfactant were used to improve its porosity and physico-chemical properties. The electrolyte material was calcined at 800°C, the crystalline nanostructures and microstructures were characterized by X-ray diffraction spectroscopy and high resolution transmission electron microscopy. The electrochemical properties were characterised by using Kittec Squadro SOFC testing equipment with air and hydrogen as gases used. These results show that the nature of the surfactant influenced the particle morphology, pore diameter, pore size, crystallite size, surface area and electrochemical properties.

Keywords: Solid oxide fuel cell; Cerium; Samarium; Surfactant; Air; Sol-gel technique.

Introduction

Sol-gel technique is a unique and adaptable technique frequently used to produce ceramic oxide materials and perovskite materials with controlled structure [1,2]. These materials are produced by two methods, the hydrolysis of the metal alkoxide precursor and its condensation [3] and aggregation of aqueous colloidal dispersions, containing discrete particles which lead to formation of materials with tailored microstructure [4,5]. The addition of surfactants in synthesizing metal oxides at ambient temperatures leads to production of composite materials that are homogeneously distributed throughout the resulting matrix and controls.

Fuel cell technology is a fast growing technology in the world today. Metal catalyst is a fundamental part for enhancing the performance of fuel cell reaction [6]. Metal catalyst like samarium doped ceria ($Ce_{0.8}Sm_{0.2}O_2$) (SDC) has been considered as a suitable electrolyte that can operate effectively at temperatures below 700°C. At these temperatures they possess high ionic conductivity in air, have superb redox properties and contain high density of surface oxygen vacancies, resulting from the population of mixed valence states [7-10]. They also possess better chemical compatibility with high performance cathode materials [11-13]. Operating at low temperatures the electrolyte is susceptible to reduction on the anode side and grain boundary resistance is a significant impediment to ionic conductivity [14, 15]. Hence surfactant can be used to improve its performance at these temperatures.

The surfactant used is Pluronic F-127, which has been proven to provide a better stabilization of the micelle walls, reduction in the inter-droplet exchange, resulting in the production of smaller particles, smaller crystals and avoidance of aggregation of the metallic nanoparticles into matrices [7].

Experimental methods

Starting materials

The surfactant Pluronic F-127, ceria acetylacetonate hydrate (98 % purity) and samarium acetylacetonate hydrate (97 % purity) were purchased from Sigma Aldrich chemicals, USA. The chemical reagents were used as acquired from their commercial sources without further purification.

Preparation of samarium doped ceria nanoparticles

The synthesis was carried out by adding 0.7200 g of cerium acac and 0.3250 g of

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samarium acac to 50 mL of ethanol and 15 mL of deionized water as the solvent. The mixture was stirred in an ultrasonic bath (UMC 20 Ultrasonic cleaner, 50 kHz and 220 W) for 30 mins. The mass of 2 to 5 g of Pluronic F-127 was added to each of the mixture and no surfactant was added to a sample. The mixtures were stirred using a magnetic stirrer on a hot plate for 30 mins at a temperature of 80 °C, to form a sol. The sol was left to dry in an oven for 24 hrs and then calcined using a muffle furnace (Kittec Squadro 1350) at 800 °C for 4 hrs [15,16]. Summary of the process is stated in table 1.

Table 1. Summary of the synthesis processes of $Ce_{0.8}Sm_{0.2}O_2$ and Pluronic F-127

Surfactant Name	Sample ID	Mass of Sample (g)
No Surfactant	SDC 1	No surfactant
Pluronic F127	SDC 2	2
Pluronic F127	SDC 3	3
Pluronic F127	SDC 4	4
Pluronic F127	SDC 5	5

Characterization

X-ray diffractometer (XRD) (Phillips PW 3710, 30 kV voltage and 35 mA current, Cu-Kα radiation 1.5406 Å wavelength) was used to analyze the crystallite structure, crystal size, lattice spacing and the phase present in the powder. The XRD diffractogram were recorded in the interval of $20° \leq 2\theta \leq 90°$ at a scan speed of 2 °/ min. The mean crystallite size ‘D’ was calculated using the Scherrer equation as shown in eq.1 [17,18].

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

where λ is the X-ray wavelength (1.5406 Å), β is the full width at half maximum of the diffraction line and θ is the diffraction angle. The JOEL 2100 HRTEM (200 kV accelerating voltage, beam current of 110 µA and a current density of 2.4 pA/cm^2) was used to analyse the lattice fringes, low magnification and diffraction patterns in the material. The morphology of samarium doped ceria powder was investigated with ZEISS FEGSEM Ultra Plus scanning electron microscopy and the samples were coated with gold before the examination.

Electrochemical characterisation

The symmetrical cell was tested by using a muffle furnace made by Kittec Squadro and a Nuvant potentiostat and galvanostat. These instruments were used as measuring instruments for the collection of the current and voltage data. 50 m^3/min of compressed air and 200 m^3/min of humidified hydrogen gas mixed with 20 % H_2O were passed through pipes into the cell and it was tested for 15 hrs. The discs had a total active area of 1.327 cm^2. The electrolyte was estimated to be 150 µm thick, the cathode was 100 µm thick and the anode was 100 µm thick.

The measurements were carried out at temperatures between 300 - 500 °C. The ionic conductivity was calculated using the eqs. 2 and 3 [15].

$$\sigma = \frac{l}{RS} \qquad (2)$$

Where; L is the electrolyte thickness, S is the electrode area of the electrolyte surface and R is the resistance in ohms (cell resistance).

$$\sigma = \sigma^o \, exp\left[\frac{E_a}{kT}\right] \qquad (3)$$

Where; E_a is the activation energy of conduction, T is the absolute temperature, σ^o is the pre-exponential factor, k is the Boltzmann constant.

Results and discussion

Powder XRD analysis

The XRD results of samarium doped ceria (SDC) can be seen in Figure 1. The structure system was cubic corresponding to a FCC lattice and the diffracted peaks were located at 2θ values of 28.88°, 33.43°, 47.75°, 56.56°, 59.29°, 69.54°, 76.76°, 79.12° and 88.32° that were indexed as (111), (200), (220), (311), (222), (400), (331), (420). The average crystallite sizes were 3.637 ± 0.043 nm, 5.461 ± 0.066 nm, 13.550 ± 0.191 nm, 15.950 ± 0.238 nm and 7.509 ± 0.094 nm for SDC1 to SDC5 respectively which was calculated from Scherrer equation using the most intense peak. The crystallite sizes corresponds with the particle sizes from the HRTEM images, confirming the lateral relationship between the particle sizes of the sample and its crystallite size, confirming the surfactants effect. The average lattice parameter a is 5.345 Å for CeO_2 phase and the Bravais lattice is a face centred cubic (FCC) unit cell. This was calculated using the eq. 4 [19]:

$$a = \frac{\lambda}{2} \times sin \times \sqrt{h^2 + k^2 + l^2} \qquad (4)$$

where, λ = X-ray wavelength and $\theta = 2\theta$ value/2, h, k, l values are Miller indices of particular planes in the crystal. The unit cell volume for all samples was 1.527×10^{-22} cm^3 for CeO_2 phase, this was calculated using the eq. 5.

$$\text{Unit cell volume} = (a)^3 \quad (5)$$

The density of the cell is 7.41 g/cm^3 for CeO_2 phase and the following equation was used to calculate this value.

$$\text{Density} = \frac{mass\,(unit\ cell)}{Volume\,(unit\ cell)} \quad (6)$$

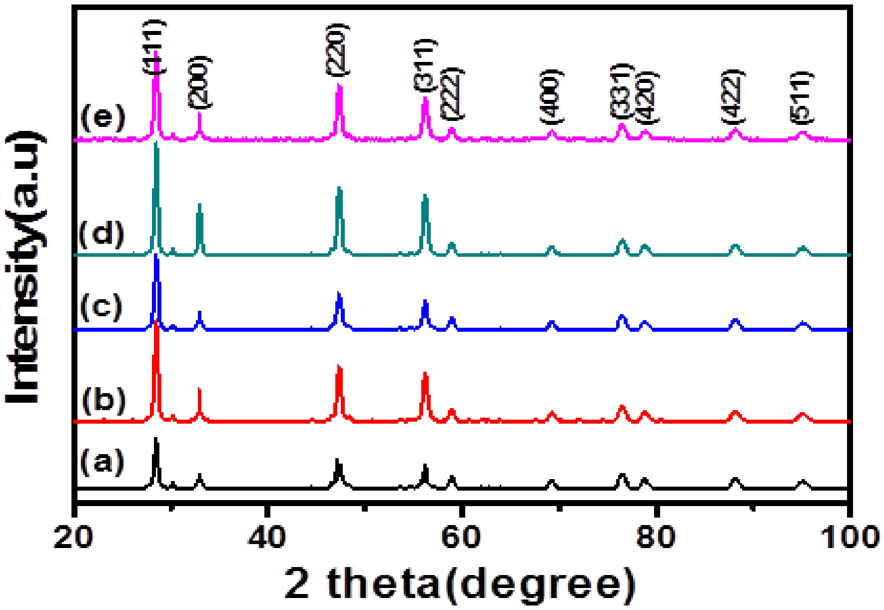

Figure 1. X-ray diffraction pattern of (a) SDC1 (b) SDC2 (c) SDC3 (d) SDC4 and (e) SDC5 calcined at 800 °C for 4 hours

HR-TEM analysis

Figure 2 shows the lattice fringes and low magnification of SDC mixed with surfactants. The lattice distance between the fringes for SDC 1 was 0.183 nm indexed to (220), SDC 2 is 0.157 nm indexed to (222), SDDC 3 is 0.202 nm indexed to (220), SDC 4 is 0.207 nm indexed to (211) and SDC 5 is 0.190 nm indexed to (220). These lattice parameters are linked to the XRD as SmO_2 structure and CeO_2 (fluorite) structures.

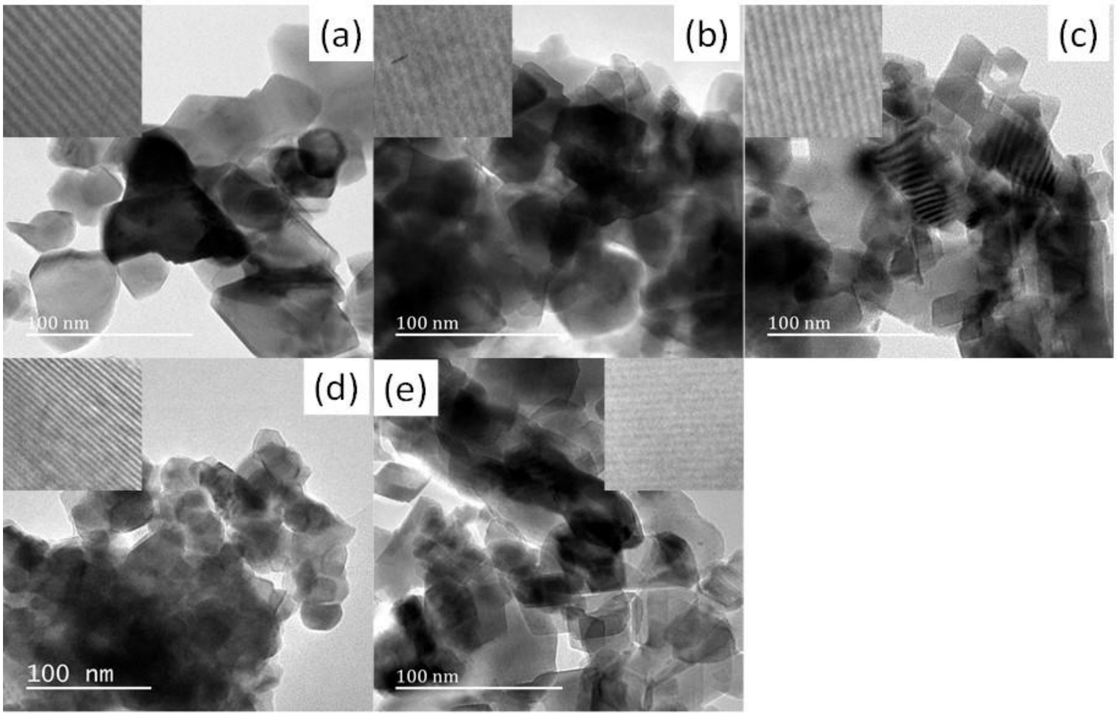

Figure 2. Low magnification and lattice fringe of the high resolution TEM for (a.) SDC1 (b).SDC 2 (c). SDC 3 (d). SDC 4 and (e).SDC 5 Calcined at 800°C for 4 hours

SEM analysis

Figure 3 show images of SDC prepared using Pluronic F-127 as surfactant, the figure reveal that particles prepared with Pluronic F-127 exposed a low conglomeration but a wide size distribution. The SEM image for all the materials synthesized, showed an accumulation of metal acacs bonded together to form agglomerates. The particles were separated as a result of the addition of surfactants, forming loosely coherent secondary loose particles.

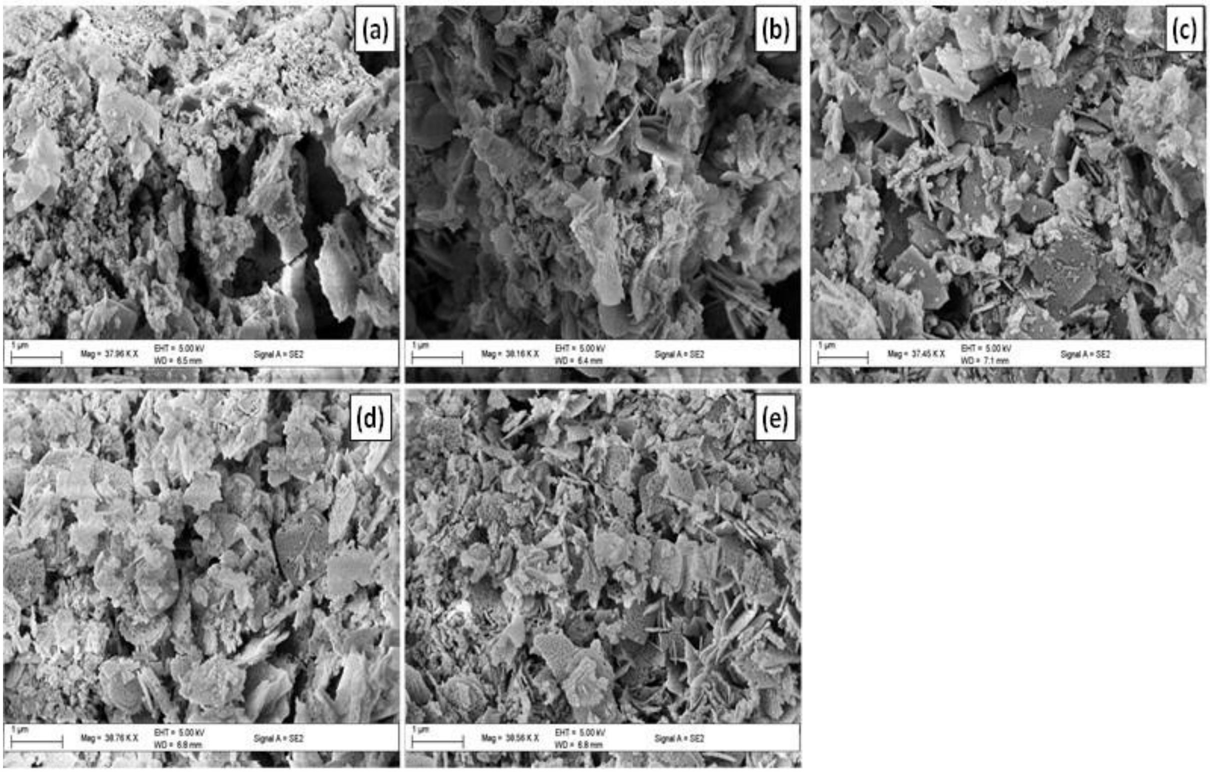

Figure 3. SEM morphology of (a) SDC 1 (b) SDC 2 (c) SDC 3 (d) SDC 4 and (e) SDC 5 calcined at 800°C for 4 hours

Electrochemical properties

Polarisation graph

Figure 4 illustrates the electrochemical property of $Ce_{0.8}Sm_{0.2}O_{2,}$ prepared using Pluronic F-127 as surfactants. The polarization properties were tested using air at the cathode side and humidified hydrogen (H_2 + 20 % H_2O) as fuel gas at the anode side. The cathode material used for testing was $Sm_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}$ perovskite with a thickness of 100 μm and the anode used was NiO/SDC which was 100 μm thick and the electrolyte was 150 μm thick. The symmetric cell was measured within the temperature intervals of 400 – 500°C. The polarization graph displayed tendencies showing a linear fall in voltage with increase in the current density. This resulted from the resistance to current flow, confirming that an increase in current is directly proportional to an increase in voltage. The open circuit voltage (OCV) showed stability for over 15 hrs at 500°C and showed different values for OCV.

The maximum power density for the SDC-surfactant samples calcined at 800°C with different wt% are shown in Figure 4. The power densities were measured at 400°C and 500°C and SDC 3 presented the maximum power density of 140.61 mW/cm^2 at 500°C and 161.24 mW/cm^2 at 400°C.

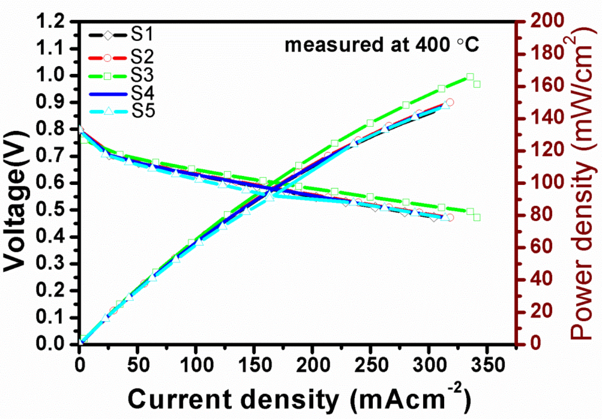

Figure 4. The polarization graph of (a) SDC 1 (b) SDC 2 (c) SDC 3 (d) SDC 4 and (e).SDC 5 calcined at 800 °C for 4 hours

Conclusions

Pluronic F-127 surfactant was mixed with SDC to improve its ability to perform better than conventional SDC in this experiment. The electrochemical properties were investigated using a potentiostat and galvanostat. The XRD revealed an increase in the crystallite sizes of the materials with surfactant when compared to the material without surfactant. SDC combined with 3 g of surfactant produced the highest power density of 161.24 mW/cm^2 and a current density of 325.90 mA/cm^2 at 400°C powered for 15 hrs. When compared to contemporary SDC without surfactant, it produced a power density of 144.289 mW/cm^2 at 400°C.

Conflict of interest

Authors declare there are no conflicts of interest.

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