Synthesis and Characterization of $\text{Ba}_{0.96}\text{Sr}_{0.04}\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_3$ Solid Oxide Fuel Cell Electrolyte by Citrate EDTA Complexing Sol-Gel Process

Jampana Madhuri Sailaja$^{1, \ast}$, N. Murali$^2$, K. Samatha$^3$, V. Veeraiyah$^4$,$^d$

$^1$Advanced Analytical Laboratory, DST-PURSE Programme, Andhra University
$^2$Department of Physics, Andhra University, Vishakhapatnam, Andhra Pradesh, India.
$^3$Department of Chemistry, Visakha University, Visakhapatnam, Andhra Pradesh, India.
$^4$School of Chemical Sciences, Orientation Foundation, Visakhapatnam, Andhra Pradesh, India.

$^\ast$madhurisailaja1981@gmail.com, $^b$muraliphdau@gmail.com,
$^c$samatha_k2002@andhrauniversity.edu.in, $^d$v_veeraiyah@yahoo.co.in

Keywords: Proton conducting electrolyte; $\text{Ba}_{0.96}\text{Sr}_{0.04}\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_3$; Sol-Gel synthesis; Fuel Cells; Raman spectra.

Abstract. This paper reports on the effect of Strontium doping on $\text{BaCe}_{0.7}\text{Zr}_{0.3}\text{O}_3$ electrolyte prepared using the citrate-EDTA complexing sol-gel process at temperature $T=1000^\circ\mathrm{C}$. The phase formation and evolution with the temperature has been studied by X-ray diffraction (XRD), thermal analysis (TG-DTA). The morphology of the sintered powder at $T=1300$ C is examined by SEM - Scanning Electron Microscopy, EDAX - Energy-dispersive X-ray spectroscopy analysis, FTIR - Fourier transforms infrared spectrometer, FTRS - Raman measurements. The crystallite size of the ceramic powders calculated from Scherrer equation is 28nm and the diffraction peak shifted to higher angles. Microstructure of the sintered powder revealed that the average grain size is in the range of 2 μm. The incorporation of Sr is found to suppress the formation of $\text{CeO}_2$ like second phase and enhance the grain growth in sintered oxides. Dense ceramic materials were obtained at 1300°C and the relative density is 80% of the theoretical density. FTIR and Raman measurements reveal the complete single phase formation of the orthorhombic perovskite structure. The ionic conductivity of the pellet is investigated from room temperature to 400 °C and is found to be 1.1x10^{-4}S/cm (400 °C). The conductivity increased as temperature increases with an activation energy of 0.48eV and hence this composition qualifies to be a promising electrolyte.

Introduction

As the energy consumption around the world is continuously rising and people’s environment –protection consciousness is growing, developing and employing clean energy source has become an interesting issue worldwide. During the past few decades, Solid oxide fuel cells (SOFCs) have been identified as future renewable energy option due to their high energy conversion efficiency, low environmental impact and high fuel flexibility [1-3]. Recently SOFCs based on proton conducting electrolytes (SOFC-H⁺) have attracted much attention due to their relatively low temperature operation (400-800°C) which helps in better sealing and interconnection of the materials and lowering the thermal expansion mismatch between the cell components [4]. But operating at such high temperatures create practical problems like high costs, material degradation, long start up and shut off periods [5,6]. To solve this problem many researchers have developed various new electrolyte materials to reduce the sintering and operating temperatures.

Perovskite—type oxides such as $\text{BaCe}_3$, $\text{BaZrO}_3$, $\text{SrZrO}_3$ and $\text{SrCeO}_3$ are known to protonic conductors among which $\text{BaCe}_3$ has highest protonic conductivity among them [7, 8]. Generally, the ceramic electrolytes are synthesized by means of solid-state reaction (SSR) method which involves extensive ball-milling, repetitive grinding and high-temperature treatment (T=1,400°C). As a result, some impurities are introduced through the heat treatment process which causes material degradation. To overcome the SSR problems, wet chemical methods (WCMs) like sol–gel, hydrothermal, co-precipitation [9-11] are adopted to obtain the desired perovskite compound. With the help of these methods fine powder morphology with less contamination can be obtained. Sol-gel and Pechini method utilizes the features of both citric acid & ethylenediaminetetra acetic acid (EDTA) to form polybasic acid chelated with various metal cations [12-13]. As a result, these
methods are able to produce a single-phase powder and dense pellet at relatively low temperature (800-1400°C). The reduction in processing temperature may be due to the sol-gel process assisted with complexing or chelating agents. The agents are able to homogenize and mix raw materials at molecular level which may increase the reaction rate and decrease the processing temperature. Details elucidation of thermal degradation characteristic of chelating agents chelates with metal cations are reported in literature [14-16]. In spite of high protonic conductivity, the chemical stability of BaCeO₃ is lesser than SrCeO₃ [17]. Therefore Sr is introduced in the A site to partially replace Ba into the perovskite structure while Ce ions are doped with Zr on the B site to improve oxide reliability in the present work.

Experimental

Powder preparation

The citrate-EDTA complexing sol-gel procedure is used for preparing Ba₀.₉₆Sr₀.₀₄Ce₀.₇Zr₀.₃O₃ oxides. The starting materials for this process are commercial Ba(NO₃)₂, ZrO(NO₃)₂·2H₂O, Ce(NO₃)₃·6H₂O, Sr(NO₃)₂ (High Media, 99.5%). Both EDTA and citric acid are added to the precursor solution as chelating agents. The molar ratio of EDTA : citric acid : the total metal cations content was set at 1:2:1. The pH value of the solution was adjusted to be around 6 using NH₄OH. The mixed solutions were heated under stirring until obtaining viscous gels at T=100°C. Additional heating at T=250°C evaporates residual water & organics, later these gels were transformed into black powders. The synthesized powder is then calcined at T=1000°C for 12h with a heating rate of 5°C/min. To obtain dense sample, the calcined powder is uniaxially pressed into cylindrical pellet under 5 ton pressures for 5min and then sintered in an air atmosphere. Sintering was carried out at T=1300°C for 5h at a heating rate of 5°C / min.

Characterization

Thermo gravimetric analysis (TGA) is performed to the dried powder (T= 250°C) by a TA instrument model SDT Q 600. The phase identification of the sintered oxides is performed with a powder Diffractometer (PANalytical X-pert Pro) with Ni filtered Cu Ka radiation and the diffraction angle from 10° to 90° with a step of 0.01°/min. Morphologies of the sintered pellet are examined using scanning electron microscope (JEOL model JSM-6610 LV) in conjunction with an energy dispersion spectrometer (EDS) to find out the percentage of elements present in the sample. A FTIR spectrometer (SHIMADZU IR Prestige-21, Singapore) is used to record the FTIR spectra of Ba₀.₉₆Sr₀.₀₄Ce₀.₇Zr₀.₃O₃ powder in the range of 400-4000 cm⁻¹ and in turn investigate the complex structure, carbonates and oxide formation. The theoretical density of the powder is calculated with the obtained XRD. FTRS-Fourier transforms Raman spectroscopy (BTC111-RAMAN-785) studies were conducted to study the vibrational modes of the samples in the range 0-1000cm⁻¹. Impedance measurements (Wayneker P6500) from room temperature to 400°C were performed within the frequency range from 20Hz to 1 MHz.

The crystallite sizes of the powder are calculated using Scherrer's formula Eq. 1.

\[ D_p = \frac{0.94\lambda}{\beta \cos \theta} \]  \hspace{1cm} (1)

where \( D_p \) = Average crystallite size, \( \beta \) = FWHM, \( \theta \) = Bragg angle, \( \lambda \) = X-ray wavelength.

The bulk density of the sintered pellet is determined using the Archimedes displacement method. In order to realize the effect of Sr doping on the structural stability, the distortion of cubic lattice was calculated based on the Goldsmith tolerance factor given by the formula Eq. 2.

\[ t = \frac{r_A + r_o}{\sqrt{2}(r_B + r_o)} \]  \hspace{1cm} (2)

where \( t \) is the tolerance factor, \( r_A \) is the ion radius of the A site where Ba²⁺(1.35Å), Sr²⁺(0.95Å), \( r_B \) is the ion radius of the B site Ce⁴⁺(0.87Å), Zr⁴⁺(0.72Å), \( r_o \) is the ion radius of the oxygen O²⁻(1.4 Å).
Results and Discussion

Thermogravimetry / Differential Thermal Analysis

To investigate the reaction of the perovskite phase structure formation, simultaneous TG-DTA curves of the sample conducted from room temperature to 1200°C are presented in Fig. 1. In terms of thermal stability nitrates are unstable than carbonate and hence are easy to decompose.

From Fig. 1 it can be seen that three regions are obtained in TG-DTA of the powder. The gradual weight loss is 17% up to 200°C and is due to absorption of water molecules. The additional weight loss along with exothermal peaks in DTA reveals that the decomposition of gel takes place in two steps. The weight loss from 250°C to 500°C is found to be 23% accompanied by a small exothermic peak at 400°C which is due to combustion of the metal nitrates. The drastic weight loss occurred from 500-630°C (25%) and the exothermic peak at T=570°C is due to co-oxidation. A very small weight loss is observed at T >1000°C which is due to barium carbonate thermal decomposition [18-19]. This is consistent with the XRD results from the Fig. 2 that Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ phase only forms upon calcining at 1000°C and above. There is no apparent weight change depicted when the temperature is higher than 1100°C, indicating complete phase formation of the compound.

Fig. 1. TG-DTA curves of Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ powder preheated at 250°C for 24h.

X-ray diffraction (XRD) analysis

The phase compositions of powder Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ have been identified by X-ray diffraction (XRD) analysis. The experimental diffraction pattern is collected at room temperature by step scanning at 0.01°/min over the range 10°≤2θ≤90°. As shown in Fig. 2 sintered oxides are predominantly the perovskite dominant structure, showing five major diffraction signals, namely those from the (002), (022), (213), (611), and (422) planes (JCPDS Card no. 22-0074). The XRD patterns of powders calcined at T=1000°C for 12 h showed a single orthorhombic phase with pnnm space group according to Knight et al. [20-22]. The cell parameters are determined by least-square refinements and the calculated lattice parameters are found to be a=8.672, b=6.147, c=6.115 and cell volume is 325.97(Å)$^3$. It was reported that phase formation in BaCeO$_3$ obtained from solid state synthesis requires calcinations at 1100°C or 1200°C for 10h or more [18,19]. Such high temperatures can result in grain growth, which causes decrease in surface area of the powder and sintered density. In the present method of preparation, 1000°C is sufficient to produce a single phase material by adjusting the pH to 6 which liberates more protons from citric acid that helps to chelate
Ba ions and enhance phase formation. The small peak near 33° may be due to BaCO$_3$ which forms due to reaction of BaCeO$_3$ with CO$_2$ observed in the calcined powder and the small peak near 24° and 37° may be due to SrCeO$_3$ like phase that disappeared after sintering.

Close examination of the XRD data reveals that as Strontium is incorporated replacing some Ba in the A sites the diffraction peak shifted to higher angles and decrease of the lattice parameters is observed, which suggests a plane distance reduction (according to Bragg's law). This can be well explained by the fact that Sr$^{2+}$ has a smaller ionic radius than Ba$^{2+}$ and the appropriate doping and ordering of the atoms within the lattice reduces the strain. Thus Sr incorporation enhances structural stability against reactions with CO$_2$ that is evident from the literature [17]. However substitution of Sr has not altered the crystal structure.

The crystallite size is examined from XRD peaks based on the Scherrer equation, and the results showed that the particle size of the synthesized sample is around 29 nm.

**Fig. 2.** XRD patterns of calcined (1000°C) and sintered (1300°C) Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ oxides.

**Fig. 3.** SEM morphologies of sintered (1300°C/5h) Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ oxides.

**Fig. 4.** EDAX Analysis of sintered (1300°C/5h) Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ oxides (a)EDAX spectra (b) Elemental analysis of compound in terms of atomic weight percentage.
An increase in the tolerance factor is observed in $\text{Ba}_{0.96}\text{Sr}_{0.04}\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_3-\delta (0.8719)$ when compared to that of $\text{BaCeO}_3 (0.856)$. Electro negativity also plays a crucial role in improving the stability [20-22]. High electro negativity of the dopant /codopant reduces the interaction of the perovskite phase with acidic gases. $\text{Sr}^{2+}(0.95)$ exhibits higher electro negativity than $\text{Ba}^{2+}(0.89)$. These factors provide better stability to the composition [23].

**Microstructure**

The surface morphology of the sintered powder shown in the Fig. 3 depicts a heterogeneous distribution of grains with an average size in the range of 2-3μm. This is consistent with the fact that the grain size decreases as the ionic radius of the dopant decreases. The X-ray emission (EDAX) analysis from Fig.4a shows that only Barium, Strontium, Zirconium and Cerium elements are present and that they are found in stoichiometric proportion according to Fig 4b. In addition, no traces of impurities are found. Dense ceramic materials were obtained at $T=1300^\circ\text{C}$ and the relative density is 80% of the theoretical density.

**FTIR - Fourier transforms infrared spectroscopy**

The FTIR spectrum of the sintered powder is shown in Fig. 5. FTIR analysis is used to explain in further detail the formation of the carbonate species during heat treatment. The high intense peak near 894.6 cm$^{-1}$ may be due to the $\equiv\text{C}-\text{H}$ bond. The peak localized in the range of 1229 cm$^{-1}$ is attributed to the C-O stretch and which may be due to the complex formed from a chelation process of chelating agents, carboxyl acids and metal ions [19, 24, 25]. The bands 1553 cm$^{-1}$ may be due to the N-O asymmetric stretch of the nitrates used, as the band is nearer to the standard data peaks of IR absorption. Two weak peaks between 1000-1200 cm$^{-1}$ may be due to C-N stretch.

**FTRS- Fourier transforms Raman spectroscopy**

Raman spectra recorded at room temperature is shown in the Fig 6. Raman Spectroscopy can not only be considered as an important tool in measuring the degree of cation ordering but also used to study dynamic changes in a structure. The small peak in the range 108 cm$^{-1}$ might be assigned to the stretching mode of the carbonate ion around the strontium ion. The Raman band around 370 cm$^{-1}$ is $\text{SrCeO}_3$ like peak. A small band near 500 cm$^{-1}$ was attributed to torsional mode of the B-O bond of the B sites and between 450-550 cm$^{-1}$ is $\text{CeO}_2$ like peak [26,27]. The small peak near 708 cm$^{-1}$ can be assigned to the symmetric metal-oxygen stretching vibrations of the BO6 octahedra [29,31].

---

**Fig. 5.** FTIR spectra of sintered ($1300^\circ\text{C}/5h$) $\text{Ba}_{0.96}\text{Sr}_{0.04}\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_3$ oxides.

**Fig. 6.** Raman spectra of sintered ($1300^\circ\text{C}/5h$) $\text{Ba}_{0.96}\text{Sr}_{0.04}\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_3$ oxides.
Impedance Analysis

The impedance spectra measured in air from 200°C to 400°C in dry air is shown in the Fig.7. Theoretically the spectra comprises of three arcs of high, medium and low frequencies, corresponding to the response of bulk, grain boundary and the electrode respectively [28, 30] in the Nyquist plots (Z’ vs. Z’’). In the Nyquist plots of the present work, the high frequency semi circle related to bulk response could not be seen due to the instrumental limitations of the experimental range. Therefore, the bulk response is assigned to the high frequency intercept of the medium arc with the real axis. A comparative Bode plot (frequency is explicit) is drawn Fig.8 with log \( \omega \) on x axis versus log |\( z \)| and phase angle on y axis; an alternative to the Nyquist plot (frequency is implicit) that has the advantage of effective extrapolation of data obtained from higher frequencies. In the regions of high and low frequencies, phase angle is nearly zero and increases at intermediate frequencies as imaginary component of impedance increases.

**Fig. 7.** Nyquist plots of samples measured from different temperatures in air atmosphere 
\( \text{Ba}_{0.96}\text{Sr}_{0.04}\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_3 \) oxides.

The Arrhenius plots were obtained from the conductivity data using the Arrhenius equation given in Eq. 3.

\[
\sigma_{ac} = \sigma_o \exp \left( -\frac{E_a}{k_B T} \right)
\]  

where \( \sigma_o \) is the pre-exponential factor, \( E_a \) is the activation energy, \( k_B \) Boltzmann constant, \( T \) is the absolute temperature respectively.

In air atmosphere, the Arrhenius plot of the sample followed a linear trend from 200°C to 400°C as shown in the Fig. 9. Here, the conductivity depicted a lower value with slightly higher activation energy in air when compared to wet atmosphere as there is no presence of water for proton conduction mechanism to take place. The conductivity values of \( \text{Ba}_{0.96}\text{Sr}_{0.04}\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_3 \) are found to be \( \text{1.1x10}^{-4} \text{S/cm} \) and the conductivity increased as temperature increases. The activation energy (0.48 eV) is determined from the slope of the plot Log\( \sigma \) vs. 1000/T and is comparable with that of the reported value available in literature [30].

**Fig. 8.** Bode plot of sintered (1300°C/5h) \( \text{Ba}_{0.96}\text{Sr}_{0.04}\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_3 \) oxides.
The variation of Dielectric constant with temperature (200 °C-400 °C) and frequency (20Hz to 1MHz) is studied. From the frequency dependent plot Fig. 10 it was observed that the value of $\varepsilon_r$ decreases sharply as the frequency increases. The higher values of dielectric constant at low frequencies can be due to space charge polarization (power frequencies) which occurs due to pile up charges at the interfaces between the sample and the electrode. In low frequency regions the dipoles will get sufficient time to orient themselves completely along the field direction when the sample is subjected to an alternating field resulting in larger values of $\varepsilon_r$ of the samples. As the frequency increases further, the dipoles in the samples cannot reorient themselves fast enough in response to the applied electric field, but lags behind, resulting in the decrease in $\varepsilon_r$ of the samples up to $10^6$ Hz. From the plot of dielectric constant versus temperature Fig. 11, it was observed that as temperature increased the dielectric constant also increased. This can be explained as follows. In space charge polarization, the increase in temperature facilitates the diffusion of ions. Additionally, thermal energy may also aid in overcoming the activation barrier for the orientation of polar molecules in the direction of the field which increases the value of $\varepsilon_r$. 

![Fig. 9. Arrhenius plot of conductivity in air for samples sintered at 1300°C/5h Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ oxides.](image)

![Fig. 10. Dielectric constant vs frequency plot of sintered (1300°C/5h) Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ oxides.](image)

![Fig. 11. Variation of Dielectric constant with Temperature of sintered (1300°C/5h) Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ oxide.](image)
Fig. 12. Variation of conductivity with frequency of sintered (1300°C/5h) Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ oxide.

The frequency dependence of Ac conductivity is given by power law Eq. 4.

$$\sigma_{ac} = A_n (T) \left[ \sin \left( \frac{n-1}{2} \right) \right] \omega^s$$

(4)

where $A_n$ is a constant. The frequency dependent exponent $s$ are a characteristic parameter representing the interactions between the charges, electrons and impurities. It has a relation with the temperature of the material ($T$) and varies between 1 and 0; the value of ideal Debye samples is equal to 1. A plot of log $\sigma_{ac}$ versus log $\omega$ Fig. 12 is a straight line with a slope $s$ which can be associated with the short range hopping of charge carriers or with extrinsic dipoles that arise from presence of defects and impurities and has a relation to doping and stoichiometry of the compound [32]. The conductivity and activation energy values determined in the present work with reference to other works are listed in the Table 1.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sintering Temperature</th>
<th>Conductivity (S/cm)</th>
<th>Activation energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCeO$_3$</td>
<td>1300°C/2hrs</td>
<td>5.13x10$^{-5}$ (500°C)</td>
<td>0.70</td>
<td>[30]</td>
</tr>
<tr>
<td>Ba$<em>{0.9}$Sr$</em>{0.1}$CeO$_3$</td>
<td>1300°C/2hrs</td>
<td>2.55x10$^{-4}$ (500°C)</td>
<td>0.61</td>
<td>[30]</td>
</tr>
<tr>
<td>BaCe$<em>{0.95}$Y$</em>{0.05}$O$_{3-δ}$</td>
<td>1550°C/10hrs</td>
<td>1.9x10$^{-3}$ (800°C)</td>
<td>0.15</td>
<td>[15]</td>
</tr>
<tr>
<td>BaCe$<em>{0.8}$Zr$</em>{0.1}$Nb$<em>{0.1}$O$</em>{3-δ}$</td>
<td>1500°C/24hrs</td>
<td>5.6x10$^{-4}$ (500°C) wet H$_2$</td>
<td>0.19</td>
<td>[33]</td>
</tr>
<tr>
<td>BaZr$<em>{0.8}$Y$</em>{0.2}$O$_{3-δ}$</td>
<td>1400°C/10hrs</td>
<td>1.17x10$^{-6}$ (400°C)</td>
<td>0.41</td>
<td>[34]</td>
</tr>
<tr>
<td>Ba$<em>{0.96}$Sr$</em>{0.04}$Ce$<em>{0.7}$Zr$</em>{0.3}$O$_3$</td>
<td>1300°C/5hrs</td>
<td>1.1x10$^{-4}$ (400°C)</td>
<td>0.48</td>
<td>This work</td>
</tr>
</tbody>
</table>

Conclusions

Ba$_{0.96}$Sr$_{0.04}$Ce$_{0.7}$Zr$_{0.3}$O$_3$ has been successfully synthesized using the citrate-EDTA complexing sol-gel process at low temperature as low as $T$=1000°C. The sample showed single phase orthorhombic structure with pmna space group and is consistent with the standard JCPDF data. The crystallite size of the ceramic powders calculated from Scherrer equation is found to be 28nm and the diffraction peaks shifted to higher angles. The microstructure of the sintered powder revealed that the average grain size is in the range of 2μm. The Sr incorporation is found to suppress the formation of CeO$_2$ like second phase and aid in increasing the grain growth of sintered oxides. Dense ceramic materials were obtained at 1300°C and the relative density is 80% of the theoretical density. FTIR and Raman measurements reveal the complete orthorhombic perovskite structure single phase formation. The ionic conductivities of the pellet are investigated from room temperature to 400°C and the value at 400°C is found to be 1.1x10$^{-4}$ S/cm. The conductivity
increased as temperature increases and the activation energies is 0.48 eV. From the above results it is proved that this method of preparation yields good electrolyte which exhibited enhanced conductivity value at low sintering temperature with increased density. Further increase in sintering temperature may increase the density, but there is a chance of evaporation of Ba at high temperatures. Further research on using of sintering aid to obtain dense samples without rise in sintering temperature along with trivalent dopant is under process.

Acknowledgements

The authors wish to thank the Coordinator DST-Purse programme, Advanced Analytical laboratory, Andhra University for providing XRD, SEM, FTIR and LCR measurements used in this work.

References


[19] R.R Chien et al., Synthesis and characterization of proton-conducting Ba(Zr$_{0.8-x}$Ce$_x$Y$_{0.2}$)O$_2.9$ ceramics, Solid State Ionics. 181 (2010) 1251-1257.


[24] H. Ding, X. Xue, BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3.5}$ electrolyte-based solid oxide fuel cells with cobalt-free PrBaFe$_2$O$_{5+d}$ layered perovskite cathode, J. Power Sources. 195 (2010) 7038-7041.

[25] S.U. Dubal et al., Proton conducting BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.2}$O$_{2.9}$ thin films by spray deposition for solid oxide fuel cell, Appl. Surf. Sci. 324 (2015) 871-876.

[26] Y. Okuyama et al., Incorporation and conduction of proton in SrCe$_{0.9-x}$Zr$_x$Y$_{0.1}$O$_{3.5}$, Solid State Ionics. 275 (2015) 35-38.


[33] Y.M. Al-Yousef, M. Ghouse, Synthesis of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (BSCF) Nanoceramic Cathode Powders by Sol-Gel Process for Solid Oxide Fuel Cell (SOFC) Application, World Journal of Nano Science and Engineering. 1 (2011) 99-107.