CHAPTER – V

STUDIES ON THE SYNTHESIS AND CHARACTERIZATION OF ZIRCONIA (Zr\(^{4+}\)) DOPED CERIUM OXIDE

5.1 Introduction

Solid oxide fuel cells (SOFCs) have emerged as promising candidate for clean and high efficient power generation system due to their high power conversion efficiency from chemical to electrical energy and its fuel flexibility. The electrolyte is an indispensable component in fuel cells, which plays a vital role in the performance of the cell [1-2]. At present, yttrium stabilized zirconia (YSZ) is most widely used as a standard electrolyte for SOFC’s. However, it operates only at a significant temperature of 1000 °C to obtain the required high oxide ion conductivity. The high operating temperature will leads to various problems such as limiting of materials selection, degradation of SOFC performance, reduction of lifetime and high fabrication cost. Which is strongly hindered the large scale production and commercial application of the cells. It is necessary to develop other cheaper materials with the temperature to intermediate or lower operating temperature (500-800 °C) for SOFC’s [3]. Thus, the low operating temperature range significantly broadens the choice of materials, reduce the cost of materials processing and device fabrications. More recently, ceria based solid electrolytes have drawn enormous attention for the applications in SOFC’s operating at intermediate temperature (IT-SOFCs) due to its high oxygen ion conductivity when compared to YSZ [4]. In this connection, there are some limitations for pure ceria to obtain high oxide ion conductivity, because of the pure ceria is a poor oxide ion
conductor ($\sigma_{600^\circ C} \sim 10^{-5} \text{ S/cm}$) and has the fluorite structure with oxygen vacancies ($V_O^{--}$) as the predominant oxide ion defects [5]. In order to resolve these limitations, dopants were frequently introduced in the cerium host lattice. To improve the oxide ion conductivity of ceria based solid electrolytes, pure ceria doped with various ions such as $\text{Zr}^{4+}$, $\text{Pr}^{3+}$, $\text{Sm}^{3+}$, $\text{Gd}^{3+}$ and $\text{Y}^{3+}$ etc. at different concentrations [6-7]. High doping concentration may lead to high conductivity, it means high defect concentrations and large carrier scattering which is a nature of obstruction to achieve a high oxide ion conductivity [8]. Among the above various ions, the incorporation of $\text{Zr}^{4+}$ ions in cerium host tends to high oxygen storage capacity, high oxide ion conductivity, greater thermal stability, high fracture toughness and chemical stability [9-11].

This present study deals with the current advancement and investigates the significance of cerium zirconium oxide as an electrolyte for SOFC applications. Conventionally high temperature synthesis is a problem for energy saving and also at high temperature the surface area of materials is low. Thus, the solid electrolytes were synthesized by simple, low cost, low temperature and environmentally benign sol-gel via hydrolysis process [12]. It is a popular technique to synthesize the materials with uniform, small particle size and various morphologies. Single phase of the materials can be achieved at low temperatures with high homogeneity. Present chapter deals with the aim to develop new ceria based zirconia solid electrolyte materials with improved electrochemical properties. Also the influence of various zirconium concentrations on the structural, optical and electrical properties of cerium oxide has been investigated. Compositions of the synthesized solid electrolytes are shown in table 5.1. Flow chart for the synthesis of cerium zirconium oxide solid electrolytes is exhibited in figure 5.1.
### Table 5.1

Compositions of the synthesized cerium zirconium oxide solid electrolytes

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZ0.2</td>
<td>$\text{Ce}<em>{0.8}\text{Zr}</em>{0.2}\text{O}_{1.9}$</td>
</tr>
<tr>
<td>CZ0.3</td>
<td>$\text{Ce}<em>{0.7}\text{Zr}</em>{0.3}\text{O}_{1.85}$</td>
</tr>
<tr>
<td>CZ0.4</td>
<td>$\text{Ce}<em>{0.6}\text{Zr}</em>{0.4}\text{O}_{1.8}$</td>
</tr>
</tbody>
</table>

**Fig. 5.1 Flow chart for the synthesis of cerium zirconium oxide solid electrolytes**

Cerium Nitrate
$(\text{Ce(NO}_3)_3 - 0.1 \text{ N}$

Zirconium Chloride
$(\text{ZrCl}_4 - 0.1 \text{ N}$

Hydrolysis for 60 hours

Solution is mixed with Ammonium hydroxide

Precipitation

Washed and dried

Fine cerium oxide

Fine zirconium oxide

CZ0.2 - $(\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_{1.8})$

CZ0.3 - $(\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_{1.85})$

CZ0.4 - $(\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_{1.8})$

Ground for 10-12 hours and annealed upto 600$^\circ$ C
5.2 Results and discussion

5.2.1 Powder X-ray diffraction studies

The structural impact of zirconium oxide on cerium lattice was assessed by powder X-ray diffraction studies. X-ray diffraction patterns of the synthesized cerium zirconium oxide annealed at 600 °C for 2 h are shown in figure 5.2. It can be clearly seen that the peaks are sharper in CZ0.2 and increases in nanocrystalline nature with increasing zirconium concentration. Thus, the observed behavior has been matched to “disturbance” of the host structure when dopants are frequently introduced. The diffraction peaks of the synthesized pure CeO\textsubscript{2} are in good agreement with the diffraction planes of nanocrystalline CeO\textsubscript{2} (JCPDS no. 34-0394) with cubic fluorite structure of Fm\textbar m symmetry.

![Figure 5.2 XRD patterns of cerium zirconium oxide solid electrolytes](image)

Figure 5.2 XRD patterns of cerium zirconium oxide solid electrolytes
In case of cerium zirconium oxide, both cubic and tetragonal phases of CeO$_2$ and ZrO$_2$ are evident [13]. In this connection, diffractograms were fitted by Rietveld refinement method to confirm the phase formation and it was shown in figure 5.3. Lattice parameters, unit cell volume and atomic positions for all the solid electrolytes were obtained by Rietveld refinement, which was calculated by means of the JANA 2006 software. It explained the presence of distinct phases, confirming the occurrence of CeO$_2$ with cubic structure as the major phase which indicates the cerium and zirconium ions are uniformly distributed to forming a solid solution. It is observed that all synthesized solid electrolytes exhibited reasonable values for the indices of refinement representing that the refinement was successful because of small mismatch between experimental and theoretical curve and high goodness of fitting [14-15].
Figure 5.3 Rietveld refinement of cerium zirconium oxide solid electrolytes

The calculated lattice parameters of CZ0.2, CZ0.3 and CZ0.4 are 5.5183, 5.4459 and 5.4372 Å respectively. The increase in addition of Zr$^{4+}$ ions on Ce$^{4+}$ lattice reduces the lattice parameter and it may be due to the redistribution of charge density. Figure 5.2 exposes the CZ0.4 (1 1 1) peak slightly shifted to higher angle of 2θ compared to that of CZ0.2 and CZ0.3 indicating the shrinkage of lattice cells which can be due to the partial substitution of larger
cerium ions (0.97 Å) by smaller zirconium ions (0.84 Å) in the structure [16]. This shrinkage of the cubic lattice cell must result in a crystalline structure deviation that strongly favors the formation of defects and increase the oxygen mobility by releasing the structural stress or microstrain induced by the shrinkage [17]. Diffractograms shows the peaks are quite broad, which indicates the smaller crystallite size of the synthesized solid electrolytes. The calculated average crystallite size by using Debye-Scherrer’s formula was found to be 18, 14 and 11 nm for CZ0.2, CZ0.3 and CZ0.4 respectively. The introduction of tetravalent cations in the host lattice majorly resulted in decreasing particle sizes. The low crystallite size confirms the possibilities to achieve high oxide ion conductivity, because in most cases the conductivity is greatly influenced by the crystallite sizes of the annealing materials. Besides, no evidence for the presence of any secondary phases related to impurities, which confirms the purity of cerium zirconium oxide solid electrolytes.

5.2.2 Fourier transform infrared spectroscopy studies

Fourier transform infrared (FT-IR) was employed to confirm the bonding characteristics of functional groups and the formation of Zr$^{4+}$ ions in the cerium host lattice. Figure 5.4 shows the FT-IR spectra of cerium zirconium oxide for different doping concentrations annealed at 600 °C for 2 h. All the three FT-IR spectrum shows the common features of zirconium oxide and cerium oxide bond formation.
Weak peaks at 3383 – 3353 cm$^{-1}$ can be attributed to the presence of stretching vibrations of O-H associated with the hydroxyl group [18]. In addition, the peaks at 1527 and 1486-1484 cm$^{-1}$ are ascribed to the symmetric and asymmetric stretching vibrations of COO$^-$ groups [19]. The peaks at 1368-1355 cm$^{-1}$ demonstrates the presence of C-H bending vibrations. A strong band at 1120 cm$^{-1}$ and 800 cm$^{-1}$ are represents the stretching vibration modes of Ce-O. Finally a well defined characteristic absorption band observed around 480 cm$^{-1}$, which confirms the O-Zr-O vibration [20-21]. It can be noted that the absorption peak intensity of ceria is decreased slightly while increasing the concentration of zirconium in the cerium zirconium oxide solid electrolytes. FT-IR results clearly indicate the coexistence of the zirconium with ceria.
5.2.3 Optical absorption studies

UV-Vis absorption spectra were used to establish the optical properties of synthesized cerium zirconium oxide solid electrolytes. Figure 5.5 exhibits the UV-Vis absorption spectra in the wavelength range of 200-700 nm. The absorption spectra for all cerium zirconium oxide electrolytes exhibits strong absorption band below 400 nm, which may be due to the charge – transfer transition from O$^{2-}$ (2p) to Ce$^{4+}$ (4f) orbitals in cerium oxide [22]. The absorption spectrum demonstrates that red shift. As for the red shift, it could be the result of an interface polaron effect arising from electron phonon coupling [23].

![Absorption Spectrum](image)

Fig. 5.5 UV-Vis absorption spectra of cerium zirconium oxide solid electrolytes
From the all absorption data, the band gap energy ($E_g$) of the solid electrolytes was calculated using the Tauc’s equation

$$\alpha h\nu = A(h\nu-E_g)^n$$

(1)

where, $A$ is a constant value, $h\nu$ is the photonic energy, $n$ is a constant which depends on the probability of transition and $\alpha$ is the absorption co-efficient. Ceria is a direct band transition material and hence $n = 2$. Plotting $(\alpha h\nu)^2$ as a function of photon energy and extrapolating the linear portion of the curve to absorption equal to zero as shown in figure 5.6, which gives the direct band gap values of cerium zirconium oxide solid electrolytes.

![Fig. 5.6 Tauc plot of cerium zirconium oxide solid electrolytes](image)

The calculated band gap values were found in the range of 3.28, 3.26 and 3.16 eV for CZ0.2, CZ0.3 and CZ0.4 respectively. It was concluded that the increase in Zr content tends to
decrease in band gap, which may be due to the Zr$^{4+}$ ions substituted in cerium lattice creates the oxygen vacancies and favor the formation of Ce$^{3+}$ from Ce$^{4+}$. The broad absorption band and lower band gap values are the possibilities to obtain high oxide ion conductivity. Our results are in good agreement with the previous reported band gap ($E_g$) values [24-25].

5.2.4 Photoluminescence studies

Photoluminescence spectrum can be applied to disclose the charge carrier trapping, immigration and transfer, and also to understand the reality of electron-hole pair interactions in the particles. PL emission spectra for the synthesized solid electrolytes were performed in the wavelength range of 200-700 nm at room temperature and are presented in figure 5.7. The excitation wavelength of 330 nm was used to perform the emission spectrum for cerium zirconium oxide solid electrolytes. The main emission band located at 388 nm is due to the charge transfer transitions between O$^{2-}$ and Ce$^{4+}$ [26]. The peak positions of the solid electrolytes in the PL spectrum are similar, but the intensity of emission peaks is significantly changed. PL emission can be changed due to the presence of large amount of defects associated with the Zr$^{4+}$ content, which influences the particle size and level of defect. The influence of Zr$^{4+}$ ions on cerium lattice was also confirmed with XRD and UV-vis absorption studies in the previous sections. The photoluminescence is mainly dependent on the Zr$^{4+}$ content, because of its addition can cause a reduction in the defects or disorder of materials. Intensity of the PL emission decreases with the increase of Zr$^{4+}$ content, which may be attributed to the self compensation. This intensity is probably related with the structural deorganization level and the charge transfer occurring between cerium, zirconium and oxygen ions.
The energy levels of the emission bands composed of oxygen 2p states (near the valence band) and cerium 5d levels (below the conduction band); hence the oxygen vacancy mediated the emission from cerium oxide [27]. The high intensity observed in the CZ0.2 indicates the recombination rate of electron-hole pairs is very high when compared with CZ0.3 and CZ0.4. Generally, the lower PL intensity corresponds to higher conductivity because of efficient charge carrier separation and a lower recombination rate. Thus, the lower recombination rate found in the CZ0.4 system confirms its role as an electrolyte. Another emission peak observed at 520 nm is may be due to the f-f transition i.e., \(^4G_{5/2}\rightarrow^6H_{n/2}\), which is remarkably enhanced by the addition of the \(Zr^{4+}\) ions in the cerium lattice. The emission band is not due to the characteristic emission of the doping ions but might arise from the oxygen vacancy which is introduced in the cerium.
lattice to compensate the negative charges associated with the doping ions [28]. The high PL intensity may be due to the high crystalline nature of the synthesized solid electrolytes with lesser defects.

**5.2.5 SEM and TEM studies**

SEM analysis was used to investigate the detailed morphology and the internal microstructure of the synthesized cerium zirconium oxide solid electrolytes. Typical SEM micrographs of CZ0.2, CZ0.3 and CZ0.4 are shown in figure 5.8 (a), (b) and (c) respectively.

![Fig. 5.8 SEM images of (a) CZ0.2 (b) CZ0.3 (c) CZ0.4 cerium zirconium oxide solid electrolytes](image)

The dependence of the structural changes can be observed for different zirconium contents. The interparticle connectivity is looks like better, producing an agglomerated and porous structure. The observed larger grain sizes may be attributed to the larger cluster size which formed due to larger surface area of the smaller crystallites.
Fig. 5.9 HRTEM images of (a) CZ0.2 (b) CZ0.3 (c) CZ0.4 cerium zirconium oxide solid electrolytes

Typical HRTEM photographs of CZ0.2, CZ0.3 and CZ0.4 are shown in figure 5.9 (a), (b) and (c) respectively. Inset of TEM shows its respective selected area electron diffraction (SAED) pattern. TEM photographs indicate that the particles are in irregular shapes and agglomerated. The morphology clearly exhibits that the narrower particle distribution on the porous structure and the tightly packed surface morphology of the particles is a beneficial for the efficient charge carrier separation. Inset confirms the fluorite lattice structure of cerium oxide due to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes.

5.2.6 AC impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful technique, which can be used to identify the characteristics, kinetics of electrochemical process and also to prove the oxide ion conductivity of the synthesized solid electrolytes. In earlier studies, the oxide ion conductivity of ceria is related with the annealing temperature, microstructures, oxygen partial
pressure in the surrounding gas atmosphere, the type and concentration of dopants. A plot is
drawn between the real part ($Z'$) and the imaginary part ($Z''$) of impedance, which is denoted as
Nyquist plot. Typical Nyquist representations of cerium zirconium oxide solid electrolytes
prepared by doctor bladed method and measured at room temperature in air atmosphere are
shown in figure 5.10.

![Nyquist plot representations of cerium zirconium oxide solid electrolytes](image)

Fig. 5.10 Nyquist plot representations of cerium zirconium oxide solid electrolytes

Small incomplete depressed arcs at high frequencies and large incomplete depressed arcs
at low frequencies can be clearly seen in the Nyquist plots. In order to clear view of the
contribution of grains, the datas are plotted on an expanded scale in the insets. Small depressed
arcs at high frequencies represent the parallel connection of charge-transfer resistance and
interfacial capacitance at the counter electrode. High frequency depressed arcs corresponding to
grain resistance \( (R_g) \) and low frequency depressed arcs corresponding to grain boundary resistance \( (R_{gb}) \). Here, depressed arcs corresponding to grain and grain boundary conductivities are highly overlapped which may be due to the similar relaxation time of charge carriers inside grain and grain boundaries. Total resistance \( (R_t) \) of the system is given by \( R_{total} = R_g + R_{gb} \), where \( R_g \) and \( R_{gb} \) are the resistances of the grain and grain boundary, respectively. In the present investigation, the equivalent circuit model approach has been used for data analysis to calculate the resistance of grain and grain boundary responses. Inset of figure 5.10 shows the equivalent circuit model \( (R_s (CPE-R)(QR)(CR)) \) [29] was used to fit the impedance data to calculate grain \( (R_g) \) and grain boundary \( (R_{gb}) \) resistance. \( R_s \) represent the solution resistance. The ChiSqr \( (\chi^2) \) for fitting EIS data using \( (R_s (CPE-R)(QR)(CR)) \) with Z simpwin software is \( 9.66 \times 10^{-5} \), which indicates the error is quite small. In some cases, the use of a single capacitor is not adequate to model the electrical response of the materials is due to the depression of arcs. For this intention, a constant phase element was used to fit the results. A constant phase element is equivalent to distribution of capacitor is parallel [30].

The total oxide ion conductivity \( (\sigma) \) is calculated from the grain resistance \( (R_g) \) and grain boundary resistance \( (R_{gb}) \), using thickness of the sample \( 't' \) and most common area covered by the electrodes in contact with the sample \( 'A' \) by using the following relations

\[
R_t = R_g + R_{gb} \quad \text{(2)}
\]

\[
\sigma = \frac{t}{R_tA} \quad \text{(3)}
\]

Total oxide ion conductivity of the cerium zirconium oxide prepared by doctor bladed method was calculated and listed in table 5.2.
Table 5.2

Total conductivity for cerium zirconium oxide solid electrolytes prepared by doctor bladed method and measured at air atmosphere

<table>
<thead>
<tr>
<th>Composition</th>
<th>Total conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZ0.2</td>
<td>$1.02 \times 10^{-5}$</td>
</tr>
<tr>
<td>CZ0.3</td>
<td>$1.32 \times 10^{-5}$</td>
</tr>
<tr>
<td>CZ0.4</td>
<td>$1.72 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Highest value of grain and total oxide ion conductivity was achieved in the CZ0.4 system due to the increase in Zr$^{4+}$ content. The smaller arc radius on the impedance spectra for grain response reflects the higher efficiency of charge transfer occurring on the surface of electrode. The lower value of grain resistance indicates the possibility to attain high oxide ion conductivity, but the grain boundary resistance limits the total oxide ion conductivity in the system. Grain boundary conductivity mainly depends on the synthesis method, space charge layer near grain boundary and Zr$^{4+}$ ions segregating at grain boundary. Further to check its suitability as an electrolyte material for intermediate SOFCs, the conductivity was observed at various temperatures. The solid electrolytes of cerium zirconium oxide were made in the form of pellets (~10 mm dia X 1.3 mm thickness) and sintered around 1200 °C for 5 h with a relative density around 95%. Impedance spectra for cerium zirconium oxide at various temperatures in the range from 300 to 600 °C (300 to 400 °C plots was not shown) with the step size of 50 °C are exhibited...
in figure 5.11. It can be seen as the temperature increases, the hopping mechanism of thermally activated ions also increases. Therefore the impedance becomes decreases.

Fig. 5.11 Impedance spectra of cerium zirconium oxide solid electrolytes sintered at 1200 °C at various temperatures in air atmosphere
Figure 5.12 shows the Arrhenius plots of log $\sigma_t$ vs. $1000/T$. The activation energy for conduction is obtained by plotting the conductivity data in the Arrhenius equation for thermally activated conduction.

$$\sigma = \sigma_0 e^{-E_a/KT}$$  \hspace{1cm} (4)

where $\sigma$ is the electrical conductivity of the solid electrolytes, $\sigma_0$ is the pre-exponential factor, $E_a$ is the activation energy for an oxide ion migration, $K$ is the Boltzmann constant and $T$ is the absolute temperature [31]. It can be noted from the above equation, conductivity can be enhanced either by increasing $\sigma_0$ or decreasing $E_a$. Similar, conductivity properties of CZ0.2, CZ0.3 and CZ0.4 were observed due to increase in temperature which results in the increase of oxygen ion mobility. For cerium zirconium oxide system, the oxygen vacancies can produces
according to the following relation, which was written in accordance with the Kroger – Vink notation of defects

$$\text{ZrO}_2 \overset{\text{CeO}_2}{\longrightarrow} \text{Zr}^{\text{ce}} + 2\text{O}^\cdot + \text{V}_0^{\text{oo}}$$----------------------------- (5)

For this equation, oxygen ions $\text{O}^2-$ can diffuse through these vacant oxygen sites and $\text{V}_0^{\text{oo}}$ results the rise in conductivity. The conductivities are significantly enhanced in CZ0.4 solid electrolytes by increasing the oxygen vacancies ($\text{V}_0^{\text{oo}}$). Some conductivity values and activation energies for cerium zirconium oxide solid electrolytes were listed in table 5.3.

**Table 5.3**

*Conductivity and activation energies of cerium zirconium oxide solid electrolytes*

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Conductivity (S/cm)</th>
<th>Activation energy (E$_a$) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600 °C</td>
<td>550 °C</td>
</tr>
<tr>
<td>CZ0.2</td>
<td>1.98 X 10$^{-4}$</td>
<td>5.7 X 10$^{-5}$</td>
</tr>
<tr>
<td>CZ0.3</td>
<td>2.08 X 10$^{-4}$</td>
<td>9.09 X 10$^{-5}$</td>
</tr>
<tr>
<td>CZ0.4</td>
<td>7.45 X 10$^{-4}$</td>
<td>2.14 X 10$^{-4}$</td>
</tr>
</tbody>
</table>

The activation energy decreases with increasing Zr$^{4+}$ concentration and reaches the lowest value for the composition CZ0.4 ($E_a = 0.97$ eV & $\sigma = 7.45 \times 10^{-4}$ S/cm). These observations are in comparable with the results of Vasylyev et al [32], Martin et al [33], Venkatesh et al [34], Zhu et al [35] and Pastor et al [8] who have studied Ce$_{0.8}$Zr$_{0.2}$O$_2$, 8 mol%
yttrium stabilized zirconia (8YSZ), Ce$_{0.8-x}$Gd$_x$Sm$_{0.2}$O$_{2-\delta}$, (Ce$_{1-x}$Nd$_x$)$_{0.95}$Mo$_{0.05}$O$_{2-\delta}$ and dysprosia stabilized zirconia (DySZ) respectively. For higher concentration of Zr$^{4+}$ ions, the amount of oxygen vacancies and Zr$^{4+}$ ions on Ce$^{4+}$ lattice sites is high enough to produce the formation of dopant vacancy associations over the whole temperature and the activation energy is constant to the sum of association and migration energy ($E_a + E_m$) [36]. For lower concentration of Zr$^{4+}$ ions, the amount of oxygen vacancy is not enough for the concentration of complex defects to be significant and the activation energy is constant which are close to the migration energy ($E_m$). In addition, the conductivities of cerium zirconium oxide were based on the oxide ion radius of zirconium oxide. In this connection, the oxide ion radius of Zr$^{4+}$ is similar to the radius of Ce$^{4+}$, which gives the maximum conductivity because the maximum conductivity can be achieved due to the similar oxide ion radius as the host ion resulting in minimum association enthalpy between dopant ion and oxygen vacancy [37]. According to Kilner [38], association energy of defect pairs decreases with decreasing oxide ion radius mismatch between the dopant cation and the host cation. Hence, the oxide ion conductivity in fluorite type materials might be enhanced by decreasing the oxide ion radius mismatch. Moreover the increase in defect concentration results the decrease in grain size because the smaller grain size reduces the hopping distance of oxide ion motion and thereby has a great influence on conductivity which was discussed earlier in the XRD section. Rupp et al [39] have analyzed the activation energy decreases linearly from 1.04 to 0.77 eV with decreasing an average grain size from 76 to 29 nm. Our results are also in good accordance with this observation.

5.2.7 Cyclic voltammetry

Cyclic voltammetry is an important electrochemical technique to obtain the information about the kinetics of heterogeneous electron-transfer reactions, the nature of the interactions
between different molecules at the electrode surface. The ratio of oxidation peak current is another important parameter to analyze whether the electrode process is reversible. Cyclic voltammograms for the different compositions of cerium zirconium oxide annealed at 600 °C is shown in figure 5.13 by sweeping the potential from 0 V to 2 V at a scan rate of 50 mV/s.

**Fig. 5.13 Cyclic voltammograms of cerium zirconium oxide solid electrolytes**

It denotes a single oxidation – reduction cycle composed of anodic and cathodic waves and it forms a loop like CV response. Dramatical changes were observed in the voltammogram due to the different compositions of zirconium content. The obtained voltammograms shows that the peak current is vary with different concentrations of zirconium oxide. The increase in zirconium content results the increase in current which represents the more ions can penetrate according to the higher current peak [40]. The current peak reduction may be due to the increase
of electrode resistance which was also confirmed with Nyquist representations. A smaller peak separation indicates a fast charge transfer and a better reversibility of the synthesized solid electrolytes. The oxidation peak potential for the all synthesized solid electrolytes are observed nearly at 0.26 V. The corresponding cathodic peak for CZ0.2, CZ0.3 and CZ0.4 was found at 0.4, 0.39 and 0.36 V respectively. While the electrochemical oxidation of Ce$^{3+}$ to Ce(OH)$_4$ [41] proceeds under an anodic bias, the cathodic peak potential results the Zr$^{4+}$ and e$^-$ extraction. The possible valance change of the cerium oxide from 3+ to 4+ or 4+ to 3+, it should have the ability to store more oxygen [42]. The addition of Zr$^{4+}$ ions involves in decreasing the ionic band between Ce and O and makes the motion of oxygen flexible. Most of the extraction process is faster than the insertion process and nearly 60% of the de-intercalation process was done in a shorter period. It represents the intercalation / de-intercalation process of Zr$^{4+}$ ions are reversible with decreasing of charges due to the loss of active material from the electrode surface.

5.2.8 Chronoamperometry

Chronoamperometric studies were used to investigate the current with time under potentiostatic polarization as a method to support the voltammetric results and also confirm the stability of synthesized solid electrolytes. Figure 5.14 depicts the chronoamperometric curves for the cerium zirconium oxide annealed at 600 °C was done at 0.5 V vs. RHE for 40 s.
Fig. 5.14 Chronoamperometric curves of cerium zirconium oxide solid electrolytes

It was clearly seen from the graph, the peak current decreases with increasing of time. A very quick current drop was observed at a short time period (0.17 s). This fast current drop expresses the stability of electrode surface and it was confirmed with cyclic voltammetry analysis in the previous section. While increasing the time, the current becomes stable indicating the high reaction activity which represents a persistent oxygen charge exchange reaction occurs in solid electrolytes [43-44]. He et al [45] have synthesized Rh/C and Rh/CeO$_2$/C catalysts for direct alcohol fuel cell (DAFC) applications and they observed the current stability at 600 s on both catalysts. Jaccoud et al [46] have studied the electrochemical behavior of Pt/YSZ and they attained the current stability after 150 s. Compared with these reports cerium zirconium oxide solid electrolytes have reached the current stability at a shorter period.
5.3 Conclusions

Homogeneous ceria based zirconia solid electrolytes were synthesized by sol-gel via hydrolysis process for intermediate temperature solid oxide fuel cells. Rietveld refinement confirmed the solid electrolytes are consisting of single phase with cubic fluorite structure. Higher angle shift of 2θ indicates the shrinkage of lattice cells favor the formation of defects and increase the oxygen mobility. Absorbance spectra exhibited the charge-transfer transition from O\(^{2-}\) (2p) to Ce\(^{4+}\) (4f) orbital in cerium oxide and the obtained broad absorption depicts the lower band gap values. Photoluminescence studies confirmed the impact of Zr\(^{4+}\) content on cerium oxide, because its addition can cause a reduction in the defects or disorder of solid electrolytes. SEM and TEM studies affirmed the narrower particle distribution on the porous structure and the tightly packed surface morphology of the particles is a beneficial for the efficient charge carrier separation. All the synthesized solid electrolytes possess excellent oxide ion conductivity for potential applications in intermediate region. Activation energy decreases from 1 to 0.97 eV with increasing of Zr\(^{4+}\) content. Lower activation energy was observed for CZ0.4 composition, which is due to the increase in mobility of oxygen vacancies and consequently reaches the high conductivity. Cyclic voltammetry studies demonstrate that the increase in Zr\(^{4+}\) content results in the increase of current which represents the more ions can penetrate according to the higher current peak. Chronoamperometric studies exhibits the quick current drop at 0.17 s indicates the high stability and high reaction activity of synthesized solid electrolytes.
References


