

Ionic conduction in calcium and samarium co-doped ceria/carbonate nanocomposite based electrolyte

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ABSTRACT: In this paper, the ionic conductivity of a nanocomposite electrolyte composed of calcium and samarium co-doped ceria (CSDC) and ternary carbonate was investigated. Calcium and samarium co-doped ceria ($Ce_{0.8}Sm_{0.18}Ca_{0.02}O_{2-\delta}$) was synthesised via sol-gel process. A nanocomposite electrolyte was prepared by mixing CSDC with ternary carbonate at a weight ratio of 70:30. The structure and thermal decomposition of the electrolyte were characterised by X-ray powder diffraction (XRD) and simultaneous thermal analysis (STA), respectively. The oxygen and proton ion conductivities of the composite electrolyte were measured by electrochemical impedance spectroscopy (EIS) within the temperature range of 300-600 °C. The oxygen ion (O^{2-}) conductivities at 600 °C for samples sintered at 600 and 700°C were found to be 0.30 and 0.44 S cm⁻¹, respectively. The proton ion (H^+) conductivities were found to be 0.33 and 0.41 S cm⁻¹ for samples sintered at 600 and 700°C, respectively. The composite electrolyte was stable under both oxidising and reducing atmosphere.

Keywords: Ionic conductivity, co-doped ceria, ternary carbonate, nanocomposite electrolyte, composite effect, impedance spectroscopy.

الموصلية الأيونية للالكتروليت المتراكب النانوي المكون من أكسيد السيريوم المطعم بالكالسيوم و

السماريوم/الكربونات

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المخلص: في هذا البحث تم دراسة الموصلية الأيونية للمتراكب النانوي المكون من طور السيريا المطعم بالكالسيوم و السماريوم (CSDC) و طور من الكربونات الثلاثية. مسحوق السيريا المطعم بالكالسيوم و السماريوم ($Ce_{0.8}Sm_{0.18}Ca_{0.02}O_{2-\delta}$) تم تخليقه بواسطة طريق السول-جل. الإلكتروليت المتراكب النانوي تم تحضيره بخلط 70% بالوزن من مسحوق السيريا المطعم بالكالسيوم و السماريوم مع 30% بالوزن من مسحوق الكربونات الثلاثية. التركيب البلوري و التكسير الحراري لالكتروليت تم دراستها بواسطة طيف حيود الأشعة السينية (XRD) و التحليل الحراري الأني (STA)، على التوالي. الموصلية الأيونية للالكتروليت المتراكب لكل من أيون الأكسجين و البروتون تم دراستها بواسطة تقنية المعاوقة الطيفية الكهروكيميائية (EIS impedance spectroscopy) في المدى الحراري (300-600 م°). الموصلية الأيونية للأكسجين (O^{2-}) عند 600 م° للعينات التي تم تليدها عند 600 م° و 700 م° كانت 0.30 و 0.44 سمنس سم⁻¹ على التوالي. الموصلية الأيونية للبروتون (H^+) عند 600 م° للعينات التي تم تليدها عند 600 م° و 700 م° كانت 0.33 و 0.41 سمنس سم⁻¹ على التوالي. الإلكتروليت المتراكب النانوي كان مستقرًا في كل من الوسطين المؤكسد و المختزل.

الكلمات المفتاحية: الموصلية الأيونية، السيريا المطعم، الكربونات الثلاثية، الإلكتروليت المتراكب النانوي، المعاوقة الطيفية

1. Introduction Solid state ionic conductors (SSICs) based on doped ceria are considered as promising electrolyte materials for the applications in the intermediate temperature regions. The most effective dopants for ceria (CeO_2) are samarium (Sm) and gadolinium (Gd) cations. These dopants are known to enhance the ionic conductivity of CeO_2 [1-3]. In addition, several studies have shown that the ionic conductivities of singly-doped ceria oxides such as $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) and $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) could be further improved by a co-doping strategy. Wang et al. [4] reported that Gd and Sm co-doped ceria exhibit much higher ionic conductivity compared to singly-doped ceria solid solution.

Guan et al. [5] have also investigated the co-doping effect on the conductivity of Gd-doped ceria (GDC) and it was found out that the ionic conductivity (0.013 S cm⁻¹ at 500 °C) of Gd and Y co-doped CeO_2 is three times higher than that of GDC ($Ce_{0.8}Gd_{0.2}O_{1.9}$). However, the above-studied co-dopants are very expensive. Therefore, exploring new, stable and cost-effective electrolyte materials with improved properties are of practical importance. On the other hand, calcium (Ca^{2+}), the divalent cation, is economically viable and readily available [6]. In addition, it has been reported that the grain boundary conduction in doped ceria oxides (e.g. GDC and YDC) can be enhanced by the addition of 2 mol % CaO. This

was attributed to that the presence of CaO will eliminate the impurities located at the grain boundary in particular SiO_2 [7, 8]. However, the drawbacks of the pure ceria phase, such as electronic conduction, could not be eliminated either by single- or co-doping approaches [9].

Composite solid electrolytes (CSEs) are basically heterogeneous mixtures of two or more phases with a combination of different properties including; high ionic or thermal conductivities, enhanced mechanical strength and thermal stability, etc [10, 11]. These improved properties make them promising electrolyte candidates for solid-state electrochemical cells. In recent years, doped ceria-carbonate composites are considered as promising electrolyte materials because of their advantages such as; super-ionic conductivity ($> 0.1 \text{ S/cm}$) above $300 \text{ }^\circ\text{C}$, multi-ionic ($\text{O}^{2-}/\text{H}^+/\text{CO}_3^{2-}$) conduction, fast ionic transport, thermodynamic stability and negligible electronic conduction [12-15]. Ceria-carbonate based composite electrolytes consist of a doped ceria (e.g. SDC, GDC, CDC) as a host phase and alkali carbonate (e.g., Na_2CO_3 , $(\text{Li}/\text{Na})_2\text{CO}_3$ and $(\text{Li}/\text{Na}/\text{K})_2\text{CO}_3$) as a second phase [14, 16-19]. These composite electrolyte have been successfully employed as electrolyte materials in different applications including; low temperature/intermediate ($300\text{--}600 \text{ }^\circ\text{C}$) solid oxide fuel cells (IT/LT-SOFCs) [9, 20, 21], water (steam) electrolysis [22], direct carbon fuel cells (DCFCs) [23, 24], carbon dioxide (CO_2) permeation membrane [24], and electrochemical synthesis of ammonia [25, 26]. In the composite electrolyte, the conductivity enhancement is believed to be due to the composite effect [20, 21, 27]. In addition, the presence of the carbonate as the second phase is found to suppress the electronic conduction of the pure ceria phase that is caused by the partial reduction of Ce^{4+} to Ce^{3+} in a reducing atmosphere [20, 28]. In recent years, a combination of the two approaches (i.e. co-doping and composite effects) has been proposed to prepare materials with improved properties (e.g. high ionic conductivity). Recently, several studies have demonstrated that co-doped ceria-carbonate composite electrolytes, including $\text{Ce}_{0.8}\text{Gd}_{0.05}\text{Y}_{0.15}\text{O}_{2-\delta}(\text{Li}/\text{Na})_2\text{CO}_3$ [21], $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Nd}_{0.1}\text{O}_{2-\delta}(\text{Li}/\text{Na})_2\text{CO}_3$ [29], $\text{Ce}_{0.8}\text{Sm}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}\text{-Na}_2\text{CO}_3$ [9], $\text{Ce}_{0.8}\text{Gd}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}(\text{Li}/\text{Na}/\text{K})_2\text{CO}_3$ [30] and $\text{Ce}_{0.90}\text{Mg}_{0.06}\text{Sr}_{0.04}\text{O}_{1.90}(\text{Li}/\text{Na})_2\text{CO}_3$ [31] exhibit high ionic conductivities at low and intermediate temperatures. In this study, nanocomposite electrolyte based on Ca and Sm co-doped ceria/carbonate was prepared. The ionic conductivity of the composite electrolyte and the effect of sintering temperature on the conductivity were investigated.

2. Experimental

2.1 Chemicals

Samarium oxide (Sm_2O_3 , 99.9 %), cerium nitride hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99 %), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99 %), lithium carbonate (Li_2CO_3 , 98 %), Citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99 %), potassium carbonate (K_2CO_3 , 99

%) and ethylenediaminetetraacetic acid, EDTA, ($\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_8$, 99 %) were purchased from Alfa Aesar. Sodium carbonate (Na_2CO_3 , 99.5 %) was purchased from Sigma Aldrich. Ammonia solution (35 %) and Nitric acid (HNO_3 , 70 %) were purchased from Fisher.

2.2 Synthesis of $\text{Ce}_{0.8}\text{Sm}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$ powder

Ca and Sm co-doped ceria (CSDC) powder with a composition of ($\text{Ce}_{0.8}\text{Sm}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$) was synthesised via a combined EDTA-citrate complexing sol-gel process [32]. Sm_2O_3 , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were used as starting materials. Sm_2O_3 was dissolved in dilute nitric acid to form samarium nitrate. Calculated amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in deionised water and mixed with samarium nitrate solution. Citric acid and EDTA were then added as complexing agents, with a ratio of citric acid: EDTA: metal cations of 1.5:1:1. Dilute aqueous ammonia solution was then added to the mixed solution, to adjust the pH value to around 6. The solution was evaporated under heating and stirring on a hot-plate and then gradually changed into a brown sticky gel before complete drying, leaving a porous yellow ash. Finally, the resultant ash was ground and subsequently calcined in air at $700 \text{ }^\circ\text{C}$ for 2 h, with heating/cooling rates of $5 \text{ }^\circ\text{C min}^{-1}$, to obtain a single phase of CSDC. A flow chart for the overall experiment is shown in Fig. 1.

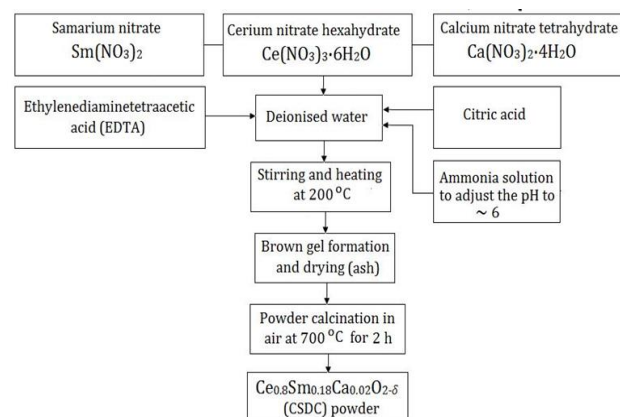


Fig. 1. A schematic diagram for the preparation of $\text{Ce}_{0.8}\text{Sm}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$.

2.3 Preparation of the composite electrolyte

The ternary eutectic salt ($(\text{Li}/\text{Na}/\text{K})_2\text{CO}_3$) was separately prepared by mixing Li_2CO_3 , Na_2CO_3 , K_2CO_3 , with a molar ratio 43.5:31.5:25 respectively. The mixture was ball milled for 9h in isopropanol at 400 rpm rotating speed using a planetary ball mill (Pulverisette 6, Fritsch). After milling, the resultant mixture is dried on a hot-plate, and then grounded and calcined in air at $600 \text{ }^\circ\text{C}$ for 1h and quenched directly to room temperature. The composite electrolyte CSDC- $(\text{Li}/\text{Na}/\text{K})_2\text{CO}_3$ was prepared by mixing CSDC powder with the ternary carbonate salt at a weight ratio (70:30). The mixture was ball milled for 9 h in isopropanol. The material was fired in air at $600 \text{ }^\circ\text{C}$ for 1 h in sequence before being quenched to room temperature. The calcined composite

electrolyte (CSDC-carbonate) was re-ground thoroughly for subsequent use.

2.4 Characterisation

2.4.1 Thermal analysis

Thermogravimetry and differential scanning calorimetry (TG/DSC) analyses were performed using a Stanton Redcroft STA/TGH series STA 1500 operating through a Rheometric Scientific system interface controlled by the software RSI Orchestrator. The thermal decomposition behaviour of the gel precursor was studied in the air from room temperature to 800 °C on heating/cooling at a rate of 10 °C/min. The thermal behaviour of the composite electrolyte was investigated in two atmospheres (air and 5% H₂-Ar) from room temperature to 600 °C with heating/cooling rates of 10 °C/min. A platinum crucible was used for carbonate containing samples.

2.4.2 X-ray powder diffraction

Phase purity of the prepared materials was studied by X-ray diffraction (XRD) using a Panalytical X'Pert Pro diffractometer with a Ni-filtered CuK α radiation ($\lambda = 1.5405 \text{ \AA}$) using 40 kV and 40 mA, fitted with an X'Celerator detector. Absolute scans were recorded in the 2θ range 5-100° with a step size of 0.0167°. The average crystallite sizes and the lattice parameters of the prepared material were estimated using Debye-Scherrer and Laue formulas as expressed by Equation 1 and Equation 2, respectively [33].

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

$$d_{hkl} = \frac{\lambda}{2 \sin \theta} \quad ; \quad a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad (2)$$

Where D is the crystallite size, λ is the wavelength of the X-ray, β is the full width at half maximum (FWHM) of the peak in radiance, θ is the Bragg angle, a is the lattice parameters, d is the interplanar distance and hkl are the Miller indices.

2.5 Pellet preparation for conductivity measurement

The AC conductivity measurements were carried out using a computer-controlled Solartron Analytical 1470E with AC amplitude of 100 mV over the frequency range 1 MHz-0.01 Hz and 10 points per decades. The composite electrolyte powder (CSDC-carbonate) was uniaxially dry-pressed at a pressure of 259 MPa into pellets with a diameter of 13 mm and thickness of ~ 2 mm. The green pellets were sintered in air at 600 and 700 °C for 2 h, at a rate of 2 °C heating/cooling. The pellets were brushed on both sides with Ag paste and fired in air at 550 °C for 30 min at a rate of 2 °C heating/cooling to form porous Ag electrodes. Pseudo 4-probe AC impedance measurements were carried out in three atmospheres namely; air and wet (~ 3% H₂O) 5% H₂-Ar. The measurements were made in cooling cycle within the temperature of 300-600 °C. The AC conductivities were calculated using Equation

3 [31]. The ionic conductivity data were fitted to an Arrhenius equation as expressed by Equation 4 [33].

$$\sigma = \frac{L}{RA} \quad (3)$$

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (4)$$

Where σ is the conductivity (S cm⁻¹), R is the resistance (Ω), L is the sample thickness (cm), A is the cross-sectional area of the specimen (cm²), σ_0 the pre-exponential factor, E_a is the activation energy (eV) k is Boltzmann constant and T is the absolute temperature.

3. Results and discussion

3.1 TGA-DSC thermal characterisation

Fig. 2 shows the thermal decomposition behaviour of the gel precursor of CSDC in air from room temperature to 800 °C. As can be seen from TGA-DSC graph, two regions of weight loss process were observed. A weight loss of about 2.64 % was observed accompanied by a small endothermic peak at 89.97 °C in the range of room temperature to 316 °C. This endothermic peak was ascribed to the loss of adsorbed water. Within the temperature range of 316 to 700 °C, a weight loss of about 4.46 % was appeared accompanied by a strong exothermic peak at 356.72 °C. This exothermic peak could be due to the pyrolysis of metal/nitrate/citrate/EDTA complexes [34]. Above 700 °C, no significant weight change was observed, thus 700 °C was chosen as the optimum calcination temperature. Moreover, the total weight loss is approximately 8.48 %.

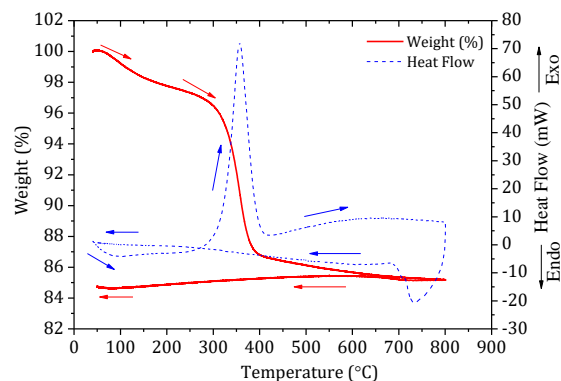


Fig.2. TGA-DSC curves of the CSDC precursor

Figs. 3a and b display the thermal behaviour of CSDC/carbonate nanocomposite electrolyte in the air and 5% H₂-Ar, respectively. It is to be noted that almost similar behaviour was observed for the composite electrolyte in both atmospheres under investigation. Upon heating, several endothermic peaks accompanied by several stages of weight loss were observed in both cases. From room temperature to 200 °C, small endothermic peaks were found. These peaks could be attributed to the loss of adsorbed water. Between 300-600 °C, strong endothermic peaks were

observed at 393.48 and 388.86 °C in air and 5% H₂-Ar, respectively. These could be due to the melting point of the ternary carbonate (400 °C) [35]. Upon cooling, only one strong exothermic event was observed at 367.12 and 340.66 °C for air and 5% H₂-Ar respectively. This can be attributed to the solidifying of the ternary carbonate. In addition, the total weight loss in the air was found to be about 0.85 and 3.63 % in air and 5% H₂-Ar, respectively. This indicates stability of the composite electrolyte in oxidising and reducing atmospheres under investigation, as confirmed by the X-ray analysis (Fig. 5).

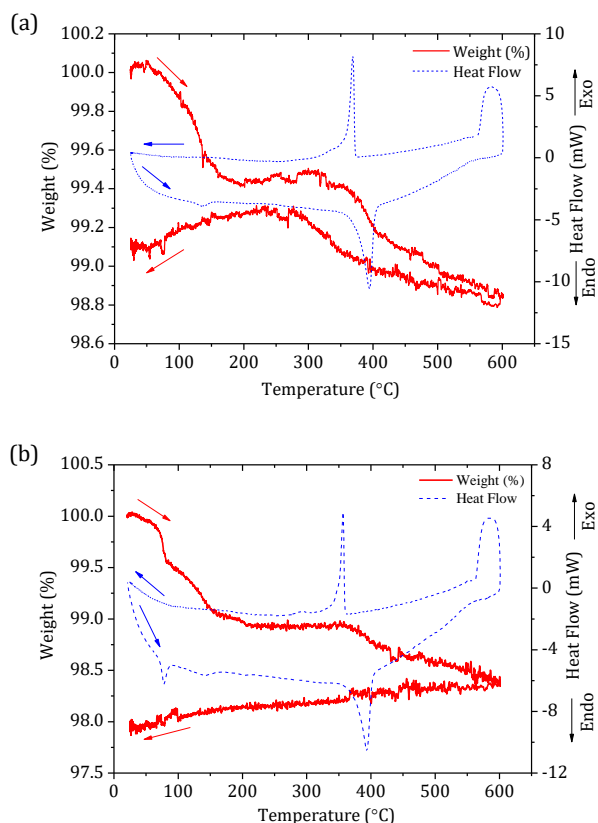


Fig.3. TGA-DSC curves of; (a) CSDC-carbonate composite in air; (b) CSDC-carbonate composite in 5% H₂-Ar

3.2 XRD analysis

Figs. 3a and b show the XRD patterns of the pure CSDC and CSDC-(Li/Na/K)₂CO₃ composite electrolyte, respectively. After firing CSDC gel precursor in air at 700 °C for 2 h, a single phase CSDC with fluorite structure was obtained, as shown in Fig. 3a. The diffraction peaks were well indexed to a cubic fluorite phase of CeO₂ (JCPDS 34-0394), indicating that Sm and Ca are well doped to the crystal structure of CeO₂. The XRD patterns of CSDC-ternary carbonate composite which was calcined in air at 600 °C for 1h and quenched directly to room temperature is represented in Fig. 3b. As can be seen, the major observed peaks could be assigned to the pure CSDC phase, whereas the small additional peaks located at 21.48°, 29.26° and 29.72° were identified as Li₂CO₃ phase (JCPDS 01-0996). This

indicates that the majority of the ternary carbonates exist as an amorphous phase in the nanocomposite electrolyte. The average crystallite sizes were found to be about 18.63±0.99 and 22.33±0.82 nm for pure CSDC and CSDC-carbonate composite, estimated from Sherrer's formula (Equation 1). The lattice parameters were determined using Laue formula (Equation 2) for cubic lattices and were $a = 5.4298 \pm 0.0031 \text{ \AA}$ and $a = 5.4326 \pm 0.0019 \text{ \AA}$ for pure CSDC and CSDC-carbonate composite, respectively. These values of lattices parameters are comparable to what has been reported earlier for Ca and Sm co-doped ceria [6, 36]. The volume of the unit cell (a^3) of CSDC was found to be 160.08±0.27 (Å)³, while that of CSDC-carbonate composite was about 160.33±0.17 (Å)³.

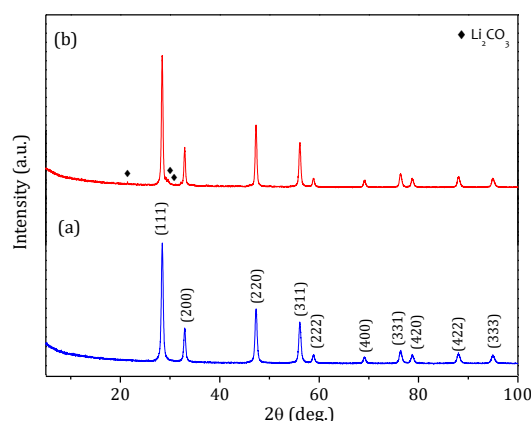


Fig.4. XRD patterns of; (a) CSDC calcined in air at 700 °C for 2 h, (b) CSDC-(Li/Na/K)₂CO₃ (70:30 wt%) calcined in air at 600 °C for 1 h

Fig. 5 displays the XRD patterns of CSDC-(Li/Na/K)₂CO₃ composite electrolyte after the thermal analysis under air (Fig. 4a) and 5% H₂-Ar (Fig. 4b) atmospheres. As can be seen, the composite electrolyte retains the fluorite structure and no phase change was observed. This confirms the stability of the composite electrolyte is in both (oxidising and reducing) atmospheres under investigation.

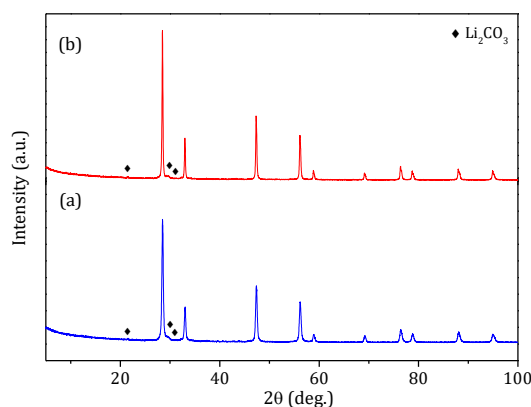


Fig.5. XRD patterns of CSDC-(Li/Na/K)₂CO₃ composite after TGA-DSC analysis; (a) in air; (b) in 5% H₂-Ar

3.4 Impedance spectroscopy and AC ionic conductivity

AC impedance measurements were carried out under two different atmospheres (air and wet 5% H₂-Ar) within the temperature range of 300-600 °C. The typical complex impedance spectra of the composite electrolyte (sample sintered at 600 and 700 °C) recorded at 400 °C in air and wet 5% H₂-Ar are shown in Figs. 6a and b, respectively. As can be seen, the CSDC-carbonate specimens (sintered at 600 and 700 °C) demonstrate a similar behaviour in both atmospheres under investigation. At high frequency, only one incomplete semicircle related to the electrolyte contribution can be resolved. These impedance spectra are comparable to those reported by Lapa et al. [17] and Chockalingam and Basu [37] for SDC-(LiNa)₂CO₃ and GDC-(LiNa)₂CO₃ respectively. At low frequency, a large tail that corresponding to the electrode processes was observed in each atmosphere. This behaviour is believed to be due to the coexistence of several processes with different relaxation times [17]. It is to be noted that the total resistance value was calculated using the high frequency intercept with real axis.

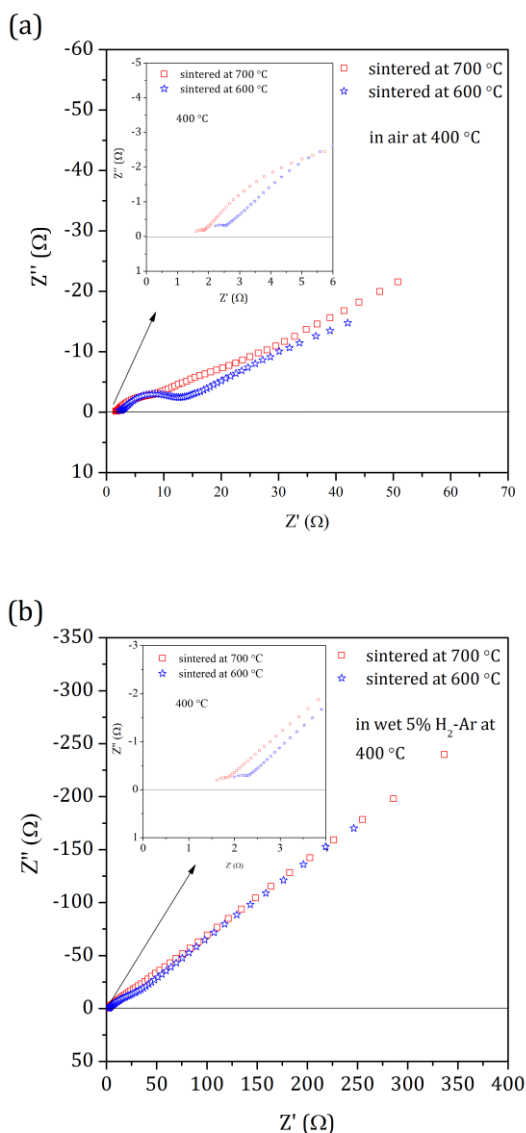


Fig.6. AC impedance spectra of CSDC-(Li/Na/K)₂CO₃ composite at 400 °C for pellets sintered at 600 and 700 °C. (a) in the air; (b) in wet 5% H₂-Ar.

The AC ionic conductivities of the composite electrolyte (CSDC-(Li/Na/K)₂CO₃) were investigated under two different atmospheres (air and wet 5% H₂-Ar). In addition, the effect of the sintering temperature on the ionic conductivities was also investigated. Figs. 7a and b show the AC ionic conductivity of CSDC-carbonate composite electrolyte (sintered at 600 and 700 °C) in the air and wet 5% H₂-Ar, respectively. As can be seen, the ionic conductivity in both cases increased with temperature. In addition, it can be clearly seen that the conductivity changed at two regions below and above ~ 375 °C, which is 25 °C lower than the melting point of the ternary carbonate (~ 400 °C). Furthermore, in both atmospheres under investigation, the sample sintered at 700 °C exhibits the highest ionic conductivity. In the air, the oxygen ion (O²⁻) conductivity is the main contributor to the overall measured conductivity. The total ionic conductivity of the sample sintered at 600 °C was changed from 1.56×10^{-4} to 0.30 S cm^{-1} in the temperature range of 300-600 °C (Fig. 7a). While the ionic conductivity of the sample sintered at 700 °C was increased from 8.52×10^{-5} to 0.44 S cm^{-1} within the same temperature range (Fig. 7a). The total ionic conductivity the composite electrolyte (0.44 S cm^{-1}) is higher than that of pure CSDC ($5.2 \times 10^{-2} \text{ S cm}^{-1}$) in the air at 600 °C [6]. Under H₂-containing atmosphere, the overall measured conductivity is mainly resulting from the proton ion (H⁺). In wet 5% H₂-Ar, within the temperature range of 300 to 600 °C (Fig. 7b), the total conductivity was increased from 1.79×10^{-3} to 0.33 S cm^{-1} , respectively, for the sample sintered at 600 °C. On the other hand, the ionic conductivity was changed from 4.51×10^{-3} to 0.41 S cm^{-1} for the sample sintered at 700 °C within the same temperature range (Fig. 7b). These values are lower than that of Ce_{0.8}Gd_{0.18}Ca_{0.02}O_{2-δ}/(Li/Na/K)₂CO₃ composite electrolyte (0.52 S cm^{-1} at 600 °C) [30]. It is to be noted, the total ionic conductivity of CSDC-carbonate composite electrolyte increased as the sample sintering temperature increased from 600 to 700 °C in both atmospheres under investigation (air and 5% wet H₂-Ar). This could be ascribed to the fact that a better contact at the interfacial region between the two phases is obtained at the high sintering temperature, which in turn provides a superionic highway for ion conduction [38]. As mentioned above, the total ionic conductivity of the co-doped ceria-ternary carbonate composite electrolyte was further enhanced above the melting point of the ternary carbonate in both atmospheres. This ionic conductivity enhancement could be due to the composite effect, which provides a fast pathway for ionic conduction. In other words, above the ternary carbonate melting point, the mobility of all ions (i.e. Li⁺, Na⁺, K⁺, O²⁻, H⁺, HCO₃⁻ and CO₃²⁻) will be enhanced, leading to a superionic conducting region at the interface between the two

phases [39]. It can also be seen from Figs. 7a and b that, at high temperature (> 375 °C), the composite electrolyte exhibits similar values of ionic conductivities under all atmospheres (air and wet 5% H_2 -Ar). However, below the melting point of the ternary carbonate, the measured conductivity in wet 5% H_2 -Ar was higher than those measured in air. This indicates that, at low temperature, proton conduction is dominant in CSDC-carbonate composite. This could be explained by the fact that proton conduction can be more easily activated at low temperature than oxygen-ion conduction [22, 40].

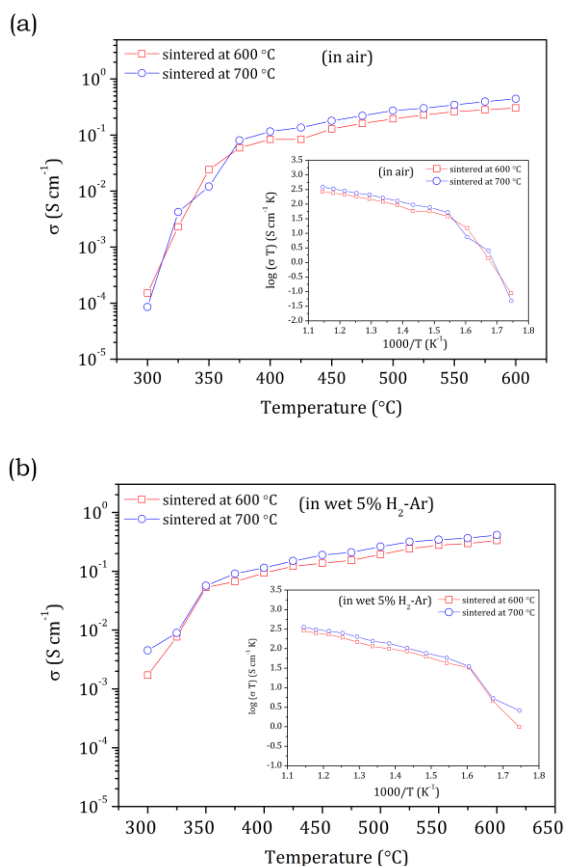


Fig.7. AC conductivity plot of CSDC-(Li/Na/K)₂CO₃ composite against temperature: (a) in air; (b) in wet 5% H₂-Ar

The activation energies (E_a) of the composite electrolyte under air and wet 5% H_2 -Ar were extracted from the slope of each series of points in the Arrhenius plots of conductivity, shown the inset of Figs. 7a and b, respectively. As can be seen, the ionic conduction of the composite electrolyte changed in two temperature regions (above and below ~ 375 °C). This indicates that there is a change in the conduction mechanism of the composite electrolyte at this temperature. The activation energies of CSDC-carbonate composite at high temperature (400-600 °C), for samples sintered in air at 600 °C or 700 °C, are listed in Table 1. It can be clearly seen from the table that the composite electrolyte (CSDC-(Li/Na/K)₂CO₃) demonstrated similar values of activation energies (~ 0.40 eV) in both atmospheres. These values are

comparable to that of CGDC-(Li/Na/K)₂CO₃ composite electrolyte [30].

Table.1 The activation energy of CSDC-carbonate composite sintered at 600 °C and 700 °C.

Sintering temperature (°C)	Activation Energy, E_a , (eV) [400-600 °C]	
	Air	Wet 5% H ₂ -Ar
600	0.43 ± 0.10	0.41 ± 0.05
700	0.43 ± 0.06	0.40 ± 0.06

Figs. 8a and b show the XRD patterns of the composite pellets sintered in air at 600 and 700 °C after the AC conductivity measurements. As can be seen, no phase change was observed after conductivity measurement in both oxidising and reducing atmospheres. This indicates the stability of the CSDC-(Li/Na/K)₂CO₃ composite electrolyte.

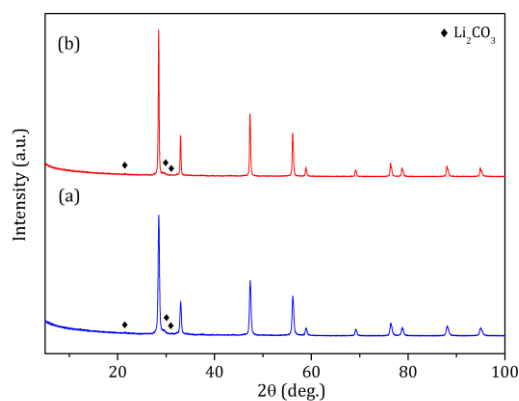


Fig.8. XRD patterns of CSDC-(Li/Na/K)₂CO₃ composite pellets after conductivity measurements; (a) sintered at 600 °C; (b) sintered at 700 °C.

4. Conclusion: In summary, Ca and Sm co-doped ceria ($Ce_{0.8}Sm_{0.18}Ca_{0.02}O_{2-\delta}$, CSDC) was successfully synthesised via sol-gel process. A nanocomposite electrolyte consisting of two phases was prepared by mixing co-doped ceria with the ternary carbonate ((Li/Na/K)₂CO₃) at a weight ratio of 70:30. The XRD results revealed that a single phase CSDC with cubic fluorite structure was obtained after calcining its dried gel in air at 700 °C for 2 h. The nanocomposite electrolyte retained its fluorite structure after the thermal and conductivity measurements in oxidising and reducing atmospheres, indicating its stability. In an air atmosphere, the ionic conductivity at 600 °C for samples sintered at 600 and 700 °C was found to be 0.30 and 0.44 $S\ cm^{-1}$, respectively. Under H_2 -containing atmosphere, the ionic conductivities were found to be 0.33 and 0.41 $S\ cm^{-1}$ for samples sintered at 600 and 700 °C, respectively. Within the temperature range of 400-600 °C, the composite electrolyte demonstrated similar values of activation energies (0.40 eV) in both atmospheres under investigation.

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