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Enhanced ionic conductivity in a composite electrolyte based on cerium oxide-ternary carbonate

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Abstract In this paper two-phase composite electrolyte composed of cerium oxide (CeO_2) and ternary carbonate ($(Li/Na/K)_2CO_3$) has been prepared by solid-state reaction. The structure and the thermal stability of CeO_2-ternary carbonate (80:20 wt%) composite were characterised by X-ray powder diffraction (XRD) and simultaneous thermal analysis (STA), respectively. The AC impedance spectroscopy and four-point DC methods have been employed to investigate the ionic conductivity in ceria-$(Li/Na/K)_2CO_3$ composite electrolyte. The ionic conductivities were carried out in two different atmospheres (air and wet 5% H_2-Ar) within the range of temperature 400-600 °C. The AC ionic conductivities of the composite electrolyte were found to be in the range of 3.45×10^{-2} to 0.248 S/cm and 5.33×10^{-2} to 0.231 S/cm at 400-600 °C in air and wet 5% H_2-Ar, respectively. Within the temperature range of 400-600 °C, the DC ionic of the ceria-carbonate composite were found to be in the range of 6.87×10^{-2} to 0.152 S/cm and 6.36×10^{-2} to 2.53×10^{-2} S/cm in air and wet 5% H_2-Ar respectively. The composite electrolyte was thermal stable in both oxidising and reducing atmosphere as indicated by thermal analysis studies.

Keywords: cerium oxide, composite effect, composite electrolyte, ionic conductivity, ternary carbonate.

الموصلية الأيونية المُحسّنة للالكتروليت المتراكب المكون من أكسيد السيريوم/الكربونات الثلاثية

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الملخص في هذا البحث تم إسبتخدام تفاعل الحالة الصلبة لتحضير الكتروليت متراكب ذو طورين و مكون من 80% بالوزن أكسيد السيريوم (CeO_2) و 20% بالوزن من الكربونات الثلاثية ($(Li/Na/K)_2CO_3$)). التركيب البلوري و ثبات الالكترويت المتراكب تم دراسته بواسطة طيف حيود الأشعة السينية (XRD) و التحليل الحراري الآني (STA) على التوالي. الموصلية الأيونية للالكتروليت المتراكب تم تقديرها بواسطة تقنية التيار المتردد للمعاوقة الطيفية (AC impedance spectroscopy) و تقنية 4–نقاط للتيار المستمر (DC four-point). الموصلية الأيونية للإلكتروليت المتراكب النانوي تم دراستها في الهواء و في الهيدروجين الرطب (wet 5% H_2-Ar) في المدى الحراري (400–600 م°). الموصلية الأيونية التي تم تقديرها بإستخدام التيار المتردد (AC conductivity) كانت في المدي مابين 3.45 × 10^{-2} إلى 0.248 سمنس/سم و 5.33 × 10^{-2} إلى 0.231 سمنس/سم في الهواء و الهيدروجين الرطب على التوالي. بيمنا كانت الموصلية الأيونية التي تم تقديرها بإستخدام التيار المستمر (DC conductivity) في المدى مابين 6.87 × 10^{-2} إلى 0.152 سمنس/سم و 6.36 × 10^{-2} إلى 2.53 × 10^{-2} سمنس/سم في الهواء و الهيدروجين الرطب على التوالي. النتائج المتحصل عليها تشير إلى ان الالكتروليت المتركب مستقر في كل من الوسط المؤكسد و المختزل.

الكلمات المفتاحية: أكسيد السيريوم، تأثير المتراكب، الالكتروليت المتراكب، الموصلية الأيونية، الكربونات الثلاثية.

Introduction

Composite electrolytes (CEs) are basically heterogeneous mixtures of two or more solid phases. These composite materials exhibit combination of different properties including; high ionic conductivity, enhanced mechanical strength and thermal stability, etc [1, 2]. These improved properties make them promising electrolyte candidates for solid-state electrochemical cells. In recent years, ceria-salt composite based electrolytes in particular ceria-carbonate composite (3C) electrolytes have received increasing attention because of their advantages such as; super-ionic conductivity (> 0.1 S/cm) above 300 °C, multi-ionic $(O^{2-}/H^{+}/CO_3^{2-})$ conduction, fast ionic transport, thermodynamic stability and negligible electronic conduction [3-6]. In general, ceria-carbonate composite electrolytes consist of two phases including singly-doped or co-doped ceria (e.g. SDC, GDC, CDC, CGDC, CSDC) as a host phase and carbonate (e.g., Na_2CO_3, $(Li/Na)_2CO_3$, $(Li/Na/K)_2CO_3$) as a second phase [3, 5, 7-11]. In ceria-carbonate composite electrolytes, the enhanced ionic conductivity is mainly due to the fast ionic transport at the interface region between the two phases (host and second phase) [3, 12]. besides to the ionic conductivity enhancement, the addition of the carbonate phase to the conventional single phase doped cerium oxide (e.g. SDC) is found to suppress the electronic conduction in doped ceria which is resulted from the partial reduction of Ce^{4+} to Ce^{3+} in H_2-containing atmosphere [13, 14]. Ceria-carbonate nanocomposite electrolytes, owing to their aforementioned properties, have been considered as promising materials which have been employed as electrolytes in different applications including; low temperature/intermediate (300−600 °C) solid oxide fuel cells (IT/LT−SOFCs) [14-16], direct carbon fuel cells (DCFCs) [17, 18], water (steam) electrolysis [19], electrochemical synthesis of ammonia [9, 17, 18] and carbon dioxide (CO_2) permeation membrane [18].It should be noted that, the enhanced ionic conductivity and stability in the above mentioned electrolytes are obtained by combining two approaches namely; doping (singly- or co-doping) and composite effect. In recent years, a composite electrolyte based on CeO_2-Na_2CO_3 has been successfully prepared by Ristoiu et al. [20] with the aim of eliminating both the effects of dopants in ceria and the eutectic carbonates mixture effects. In the present study, a simple composite electrolyte based on pure ceria (CeO_2) as host phase and ternary carbonate ($(Li/Na/K)_2CO_3$) as second phase was developed, eliminating the dopant effect in ceria. The AC and DC ionic conductivities of the composite electrolyte were investigated in air and wet 5% H_2-Ar.

2. Experimental

2.1 Preparation of the composite electrolyte

The ternary eutectic salt was separately prepared by solid-state reaction (SSR). The carbonate salts including; Li_2CO_3 (Alfa Aesar, 98 %), Na_2CO_3 (Aldrich, 99.5+ %) and K_2CO_3 (Alfa Aesar, 99 %) were mixed with a molar ratio of 43.5:31.5:25, respectively. The mixture of the ternary carbonate was calcined in air at 600 °C for 1 h before being quenched directly to room temperature, then it was grounded thoroughly for subsequent use. The composite electrolyte was made by mixing the commercial cerium oxide (CeO_2, Alfa-Aesar, 99.9% REO) with the previously prepared ternary carbonate salt with the weight ratio of 80:20. The CeO_2-$(Li/Na/K)_2CO_3$ mixture was grounded thoroughly with an agate mortar in acetone and calcined in air at 680 °C for 1 h to ensure homogenization of the ternary carbonate with the cerium oxide particles, then the mixture was quenched directly to room temperature and re-ground for the subsequent use.

2.2 Characterization

2.2.2 X-ray powder diffraction

X-ray diffraction (XRD) data were conducted at room temperature using a Panalytical X'Pert Pro diffractometer with a Ni-filtered using CuKα radiation using 40 kV and 40 mA (λ = 1.5405 Å), fitted with a X'Celerator detector. Absolute scans were recorded in the 2θ range 5-100° with a step size of 0.0167°. The crystalline sizes of the prepared materials estimated using Debye-Scherrer formula (Equation 1) [21].

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

Where τ 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 and θ is the Bragg angle.

2.2.2 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 behaviour of the ternary carbonate eutectic salt mixture ($(Li/Na/K)_2CO_3$ 43.5:31.5:25 mol%) was investigated in air on heating from room temperature to 800 °C and cooling from 800 °C to room temperature at rate of 10 °C/min. Two different atmospheres namely; air and 5% H_2-Ar were used to investigate the thermal behaviour of the composite electrolyte on heating from room temperature to 600 °C and cooling from 600 °C to room temperature at rate of 10 °C/min. It should be noted that a platinum crucible was used as a sample container.

2.2.3 Pellet preparation for conductivity measurements

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 powder was uniaxially dry-pressed under 300 MPa into pellets of 13 mm in diameter and 2 mm in thickness and of 13 mm in diameter 10 mm in thickness for AC and four-point DC conductivity measurements respectively. The pellets were sintered in air at 700 °C for 2 h at rate of 2 °C heating/cooling. For AC condutivity measurments, the pellets were brushed onto both sides with Ag paste and fired in air at 550 °C for 30 min at rate of 2 °C heating/cooling to form porous Ag electrodes. For four-point DC configuration, four silver wires were attached to the pellet at four points using Ag paste and then fired in air at 550 °C for 30 min. AC impedance and four-point DC measurements were preformed in two atmospheres (air, and wet (~ 3% H_2O) 5% H_2-Ar). Both measurements were made in cooling cycle in the range of temperature 400-600 °C. The conductivities were calculated using Equation 2 [22].

$$\sigma = \frac{L}{RA} \qquad (2)$$

Where σ is the conductivity (S/cm), R is the resistance (Ω), L is the sample thickness (cm) and A is the cross-sectional area of the specimen (cm^2).

3. Results and discussion

3.1 XRD analysis

The XRD patterns of the ternary carbonate $(Li/Na/K)_2CO_3$, commercial cerium oxide (CeO_2) and CeO_2-$(Li/Na/K)_2CO_3$ composite electrolyte are shown in Fig. 1a-c. As can be seen from Fig. 1a, after firing the ternary carbonate in air at 600 °C for 1 h, a complicated phase composition was observed. In the case of the commercial CeO_2 (Fig. 1b), the detected peaks are indexed to a single phase CeO_2 with fluorite structure (JCPDS 34-0394). The powder XRD patterns of CeO_2-$(Li/Na/K)_2CO_3$ composite fired in air for 1 h at 680 °C are shown in Fig. 1c. As can be seen, the composite electrolyte shows the major characteristic peaks of pure CeO_2, but very small additional peaks which could be identified as Li_2CO_3 phase (JCPDS 01-0996), were observed at 29.70° and 31.30°. This indicates that the majority of the ternary carbonates exist as amorphous phase in the composite electrolyte. The crystallite size of the commercial CeO_2 is 97.73 nm, while that of CeO_2-$(Li/Na/K)_2CO_3$ composite (80:20 wt%) calcined at 680 °C for 1 h is 98.91 nm, estimated from Sherrer's formula (Equation 1).

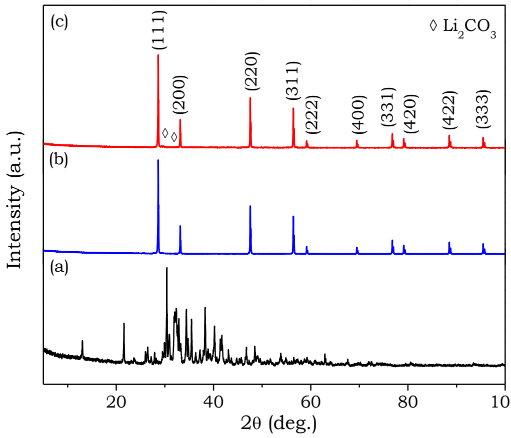


Fig.1: XRD patterns of (a) $(Li/Na/K)_2CO_3$ calcined at 600 °C for 1 h; (b) commercial CeO_2 powder; (c) CeO_2-$(Li/Na/K)_2CO_3$ composite calcined at 680 °C for 1 h.

3.2 Thermal analysis

Fig. 2 represents the TGA/DSC curves of the ternary carbonate ($(Li/Na/K)_2CO_3$ 43.5:31.5:25 mol%) in air atmosphere. Upon heating, there was no significant weight loss observed from room temperature to 400 °C. By further heating to 800 °C, weight loss, accompanied by a strong endothermic peak at ~ 402 °C, was observed, which was due to the melting point of the ternary carbonate (~ 400 °C) [23]. Upon cooling, a strong exothermic event was observed at 380.34 °C, which can be attributed to the solidifying of the ternary carbonate ($(Li/Na/K)_2CO_3$). In addition, there was a total weight loss of ~ 6.98 %. This could be related to the partial decomposition of carbonate [7].

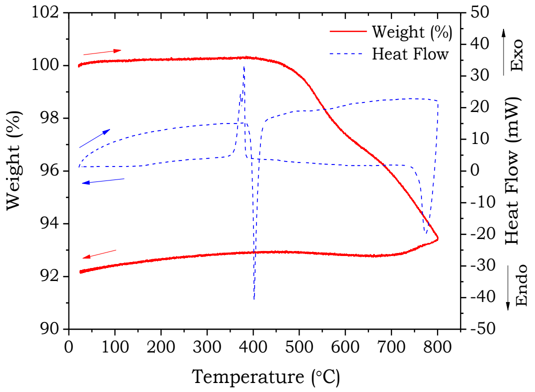


Fig.2: TGA-DSC analysis of ternary carbonate $(Li/Na/K)_2CO_3$ (43.5:31.5:25 mol%) in static air.

Fig. 3a and b represent the thermal behaviour of CeO_2-carbonate under two different atmospheres namely; air and 5% H_2-Ar, respectively. As can be seen, the composite electrolyte exhibits almost a similar behaviour in both atmospheres under investigation. In air atmosphere, upon heating, a slight weight gain of about 0.15% was observed between room temperature and 200 °C, which might be due to the buoyancy effect. In the case of 5% H_2-Ar atmosphere, within the range of room temperature to 200 °C, small endothermic peak was found which could be attributed to the loss of absorbed water. In both atmospheres, within the temperature range from 300 to 600 °C, strong endothermic peaks were observed at 401.03 and 401.59 °C in air and 5% H_2-Ar. These endothermic peaks could be ascribed to the melting point of the ternary carbonate (400 °C), as mentioned above [23]. Upon cooling, only one exothermic event was observed in each atmosphere, which can be attributed to the solidifying of the ternary carbonate. These exothermic peaks are observed at the operating temperature of 379.87 and 364.51 °C for air and 5% H_2-Ar respectively. Furthermore, the total weight losses were approximately 0.23% and 2.81% in air and 5% H_2-Ar atmospheres, respectively. This indicates the thermal stabilities of the CeO_2-carbonate composite electrolyte in the oxidising and reducing atmospheres within the measured temperature range.

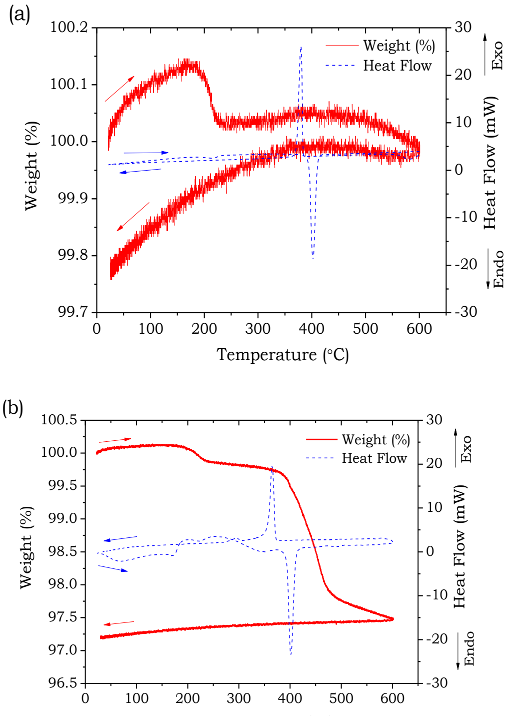


Fig.3: TGA-DSC analysis of CeO_2-$(Li/Na/K)_2CO_3$ composite. (a) in air; (b) in 5% H_2-Ar.

The XRD patterns of CeO_2-$(Li/Na/K)_2CO_3$ composite after the thermal analysis in two different atmospheres (air and 5% H_2-Ar) are shown in Fig 4a and b. As can be seen, the composite electrolyte retains the fluorite structure and no phase change was observed. This confirms that the composite electrolyte is stable in the atmospheres under study.

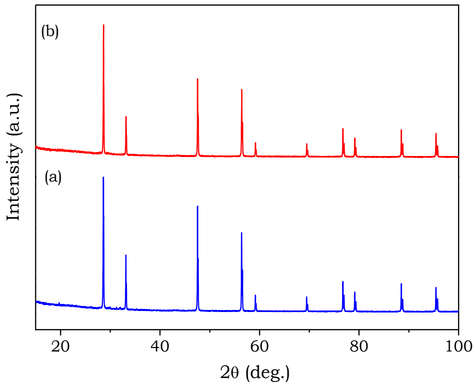


Fig.4: XRD patterns of CeO_2-$(Li/Na/K)_2CO_3$ composite after TGA-DSC analysis; (a) in air; (b) in 5% H_2-Ar.

3.4 The ionic conductivity of the composite electrolyte

The AC ionic conductivities of ceria-carbonate (CeO_2-$(Li/Na/K)_2CO_3$) electrolyte (80:20 wt%) were measured by electrochemical impedance spectroscopy (EIS) under two different atmospheres including air and wet 5% H_2-Ar within the temperature range of 400-600 °C. Figs 5 and 6 represent the typical impedance spectra of CeO_2-$(Li/Na/K)_2CO_3$ composite electrolyte at 450 °C in air and wet 5% H_2-Ar respectively. As can be seen, only small part of the high frequency semicircle which is attributed to the electrolyte contribution was observed in each of the atmospheres under investigation (Fig 5b and Fig 6b). At low frequency, a large depressed semicircle was observed in air (Fig a), while a large tail was observed in wet 5% H_2-Ar (Fig a) which are related to electrode contribution. The low frequency semicircle is usually large because the barrier between the electronic conduction in the electrode and the ionic conduction in the electrolyte [13, 24]. The high frequency intercept with real axis was used to calculate total resistance value.

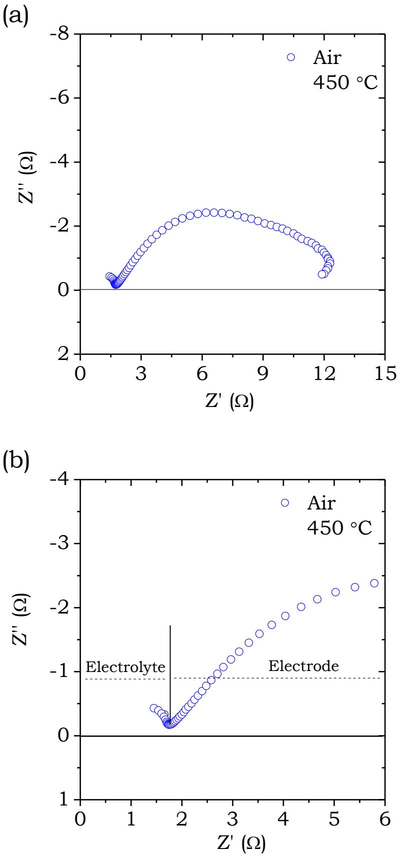


Fig. 5: (a) Impedance spectra of CeO_2-$(Li/Na/K)_2CO_3$ composite in air; (b) enlarged spectra.

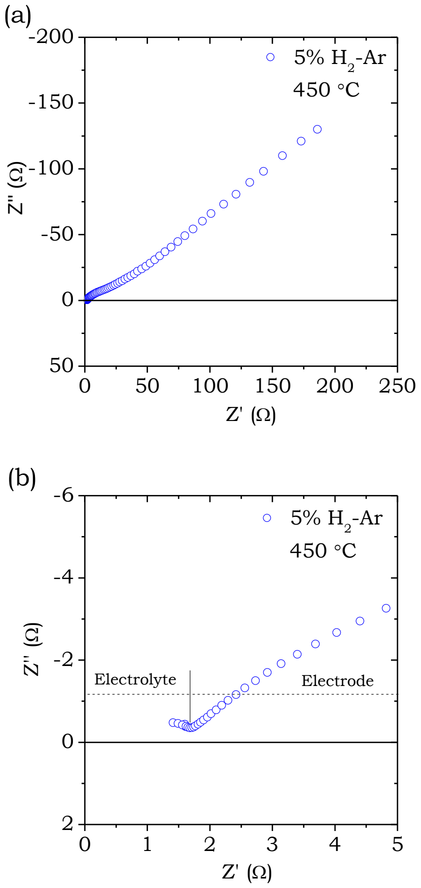


Fig. 6: (a) Impedance spectra of CeO_2-$(Li/Na/K)_2CO_3$ composite in wet 5% H_2-Ar ; (b) enlarged spectra.

Fig. 7 shows the dependence of the total AC ionic conductivities of the composite electrolyte (CeO_2-$(Li/Na/K)_2CO_3$) on the operating temperature (400-600 °C) in air and wet 5% H_2-Ar. As can be seen, the ionic conductivities of the CeO_2-carbonate composite in both atmospheres (air and wet 5% H_2-Ar) increase with increasing the temperature from 400 to 600 °C. Under air atmosphere, the oxygen ion (O^{2-}) conductivity is the main contributor to the overall measured conductivity, while the conductivity measured under H_2-containing atmosphere is mainly resulting from the proton ion (H^+) conduction. Within the temperature range of 400 to 600 °C, the total ionic conductivities are increased from 3.45×10^{-2} to 0.248 S/cm in air and from 5.33×10^{-2} to 0.231 S/cm in wet 5% H_2-Ar.

According to Zhu et al. [24], the enhancement in the ionic conductivity of ceria-composite electrolytes could be explained by the interfacial conduction mechanism. Unlike traditional single-phase electrolyte materials (e.g. YSZ, SDC), in the doped ceria-carbonate composites, the interfacial regions between the two phases provide a smooth pathway for ionic conduction. In the ceria-carbonate composite, the oxygen ion conduction (O^{2-}) occurs through ceria phase and the interface between the two phases. In contrast, the proton conduction (H^+) occurs only at the interface between the ceria and the carbonate. Protons can be transported via an intermediate carrier (HCO_3^-), formed by coupling CO_3^{2-} with H^+ [25, 26].

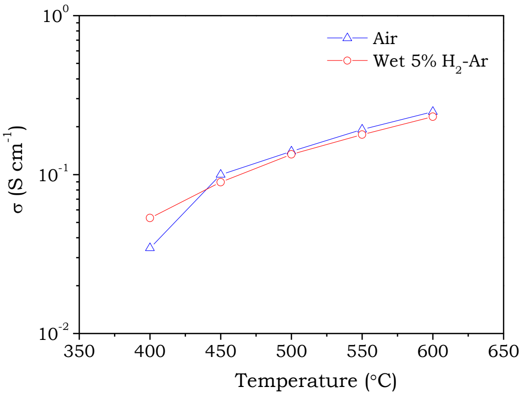


Fig. 7: AC conductivity plot of CeO_2-$(Li/Na/K)_2CO_3$ composite against temperature under air and 5% H_2-Ar.

The DC ionic conductivity was measure using four-point method within the temperature range of 400-600 °C in air and wet 5% H_2-Ar, as shown in Fig. 8. As in the case of AC conductivity measurements, the DC ionic conductivity increases with increasing temperature in both atmospheres under investigation. In air atmosphere, the ionic of the ceria-carbonate composite increased from 6.87×10^{-2} to 0.152 S/cm as the temperature increased from 400 to 600 °C. The DC ionic conductivity of CeO_2-$(Li/Na/K)_2CO_3$ composite (0.152 S/cm) is higher than that reported by Ristoiu at al. [20] for pure CeO_2 (3.5×10^{-5} S/cm) and CeO_2-Na_2CO_3 (7.3×10^{-4} S/cm) in air at 600 °C. Under wet 5% H_2-Ar atmosphere, the ionic conductivity of the composite electrolytes increased from 6.36×10^{-2} S/cm at 400 °C to 2.53×10^{-2} S/cm at 600 °C. It can be also seen from Fig. 8 that the measured DC ionic conductivity in air (oxygen ion conduction) is higher than that measured in wet 5% H_2-Ar (proton ion conduction) within the temperature range of 400-600 °C. This indicates that the oxygen ion (O^{2-}) conduction is dominant in CeO_2-carbonate composite electrolyte. Similar results in which the DC ionic conductivity in air is higher than that in H_2-containing atmosphere were reported by Abbas et al. [27] for Ca-doped ceria-binary carbonate composite electrolyte (CDC-$(Na/K)_2CO_3$). The obtained results indicate that the composite electrolyte (CeO_2-ternary carbonate) is a co-ionic (O^{2-}/H^+) conductor.

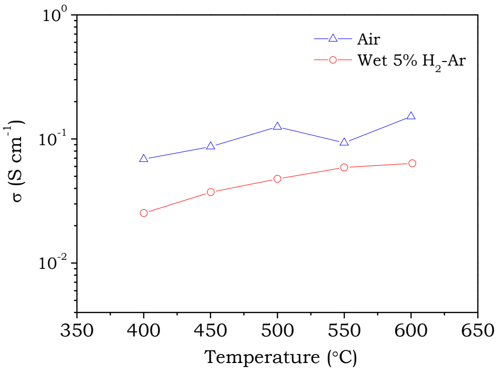
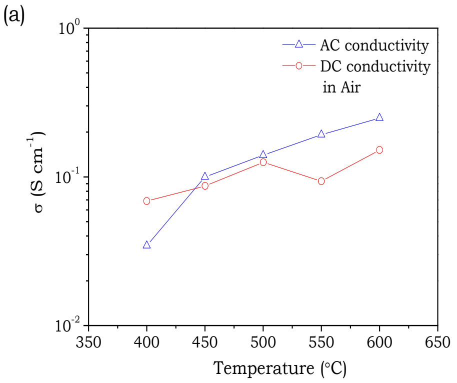


Fig. 8: DC conductivity plot of CeO_2-$(Li/Na/K)_2CO_3$ composite against temperature under air and 5% H_2-Ar.

Figs. 9a and b represent a comparison between the AC and DC ionic conductivity conductivities in air and wet 5% H_2-Ar, respectively. As can be seen, the AC ionic conductivity is higher than the DC ionic conductivity in both atmospheres under investigation (air and wet 5% H_2-Ar). This could be attributed to the fact that the AC impedance spectroscopic technique is not very suitable for studying the ionic conductivity in oxide-carbonate composite systems in which all mobile ions including; Li^+, Na^+, K^+, O^{2-}, H^+, HCO_3^-, and CO_3^{2-} will contribute to the overall measured ionic conductivity and the contribution of H^+ or O^{2-} ions cannot be distinguished. On the other hand, when using four-point DC conductivity measurement, only the contribution of O^{2-} and H^+ ions can be determined in air and H_2-containg atmosphere while the other ions are blocked at the electrodes [19, 26, 28]. This blocking effect has also been observed during the electrochemical synthesis of ammonia using ceria-ternary carbonate composite electrolyte SDC- and CGDC-$(Li/Na/K)_2CO_3$) [10, 29].



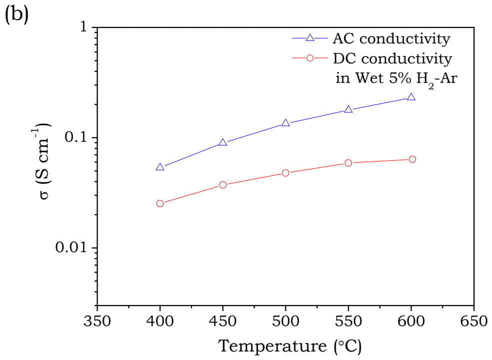


Fig. 9: comparison between of the AC and DC ionic conductivities of the composite electrolyte: (a) in air; (b) in wet 5% H_2-Ar.

The activation energies (E_a) of CeO_2-carbonate composite electrolyte in air and wet 5% H_2-Ar were extracted from the slope of each series of points in the Arrhenius plots of conductivity as shown in Figs. 10 a and b. The activation energies of ceria-carbonate composite within the range of temperature (400-600 °C), are listed in Table 1. It is to be noted that the composite electrolyte exhibit similar values of activation energies in both atmospheres under investigation. In the case of AC conductivity, the activation energies were found to be 0.40 ± 0.02 eV and 0.44 ± 0.06 eV in air and wet 5% H_2-Ar, respectively. These values are similar to that reported by Benamira at al. [7] for GDC-$(Li/Na)_2CO_3$ composite (0.40 eV), indicating the same activation mechanism. In case of four-point DC conductivity measurement, the activation energies were found to be 0.27 ± 0.16 eV and 0.33 ± 0.08 eV in air and wet 5% H_2-Ar, respectively. These values of the activation energies are comparable to that reported by Jaiswal et al. [30] for Mg and Sr co-doped ceria-carbonate composite (0.30 eV).

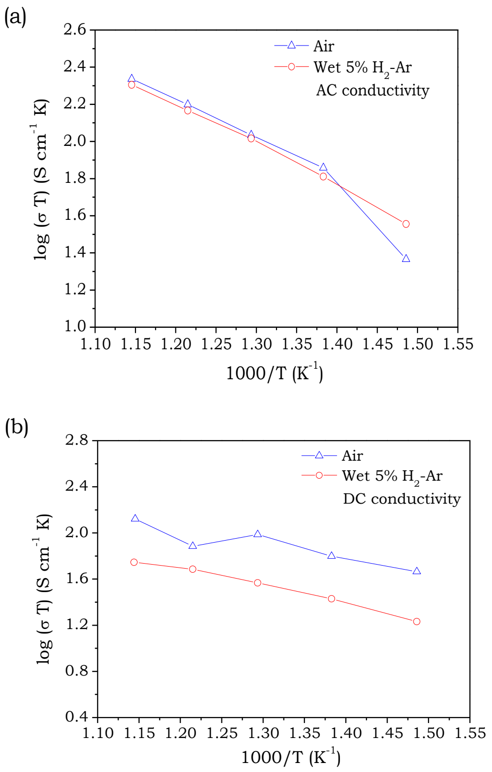


Fig. 10: Arrhenius plots of the total ionic conductivities of CeO_2-carbonate composite in air and wet 5% H_2-Ar: (a) AC conductivity; (b) DC conductivity.

Table 1: Activation energy of CeO_2-$(Li/Na/K)_2CO_3$ composite (80:20 wt%).

Atmosphere	Activation Energy, E_a (eV) (400-600 ^{0}C)	
	AC conductivity	DC conductivity
Air	0.40 ± 0.02	0.27 ± 0.16
Wet 5% H_2-Ar	0.44 ± 0.06	0.33 ± 0.08

Conclusion

In summary, two-phase composite electrolyte based on cerium oxide-ternary carbonate has been successfully prepared by mixing commercial cerium oxide (CeO_2) with the ternary carbonate ($(Li/Na/K)_2CO_3$) at weight ratio of 80:20%. The composite electrolyte was thermally stable in oxidizing and reducing atmospheres. The ionic conductivity of the composite electrolyte was measured using AC impedance spectroscopy and four-point DC techniques. The conductivity measurements were carried out in air and wet 5% H_2-Ar in range of temperature (400-600 ^{0}C). The obtained results showed that the AC ionic conductivity is higher than the DC ionic conductivity under both atmospheres under investigation. In air, the AC ionic conductivity was found to be 0.248 S/cm, while the DC ionic conductivity reached a value of 0.152 S/cm at 600 ^{0}C. In wet 5% H_2-Ar, the AC ionic conductivity was about 0.231 S/cm, whereas the DC ionic conductivity of the composite electrolyte was found to 2.53 × 10^{-2} S/cm.

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