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The ionic conductivity of a nanocomposite electrolyte based on calcium-doped ceria/ternary carbonate

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Abstract The ionic conductivity of Ca-doped ceria (CDC)-carbonate nanocomposite electrolyte was investigated. CDC powder with a composition of ($Ce_{0.8}Ca_{0.2}O_{2-\delta}$) was synthesised via a co-precipitation method and used as the host phase. Ternary carbonate eutectic salt ($(Li/Na/K)_2CO_3$) was prepared by solid state reaction and selected as the second phase. The CDC–carbonate composite was prepared by mixing CDC and ternary carbonate powders at weight ratio of 80:20. The structure of CDC powder and CDC–carbonate composite were characterised by X-ray powder diffraction (XRD). The ionic conductivities of the composite electrolyte were measured by impedance spectroscopy (IS) within the temperature range of 300–600 °C in two different atmospheres (air and wet (3% H_2O) 5% H_2–Ar). The ionic conductivity of the composite electrolyte was found to be $0.12–1.24 \times 10^{-5}$, and $0.13–7.97 \times 10^{-5}$ S cm^{-1} in air and wet 5% H_2-Ar respectively.

Keywords: Calcium doped ceria, composite effect, ionic conductivity, nanocomposite electrolyte, ternary carbonate.

الموصلية الأيونية للالكتروليت المتراكب النانوي المكون من السيريا المطّعم بالكالسيوم/الكربونات الثلاثية

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الملخص يهدف هذا البحث إلى دراسة الموصلية الأيونية للإلكتروليت المتراكب النانوي المكون من السيريا المُطّعم بالكالسيوم/الكربونات الثلاثية. مسحوق السيريا المُطّعم بالكالسيوم ($Ce_{0.8}Ca_{0.2}O_{2-\delta}$) حُضّر بطريقة الترسيب المصاحب و أُستخدم كطور مضيف. أما الطور الثاني المكون من الكربونات الثلاثية ($(Li/Na/K)_2CO_3$) فقد تم تحضيره بواسطة تفاعل الحالة الصلبة. الإلكتروليت المتراكب النانوي حُضر بخلط 80% بالوزن من مسحوق السيريا المُطّعم بالكالسيوم مع 20% بالوزن من مسحوق الكربونات الثلاثية. التركيب البلوري لمسحوق كل من السيريا المُطعم بالكالسيوم و الكربونات الثلاثية تم دراسته بإستخدام تقنية حيود الأشعة السينية (X-ray). الموصلية الأيونية للإلكتروليت المتراكب النانوي تم دراستها في الهواء و في الهيدروجين الرطب (wet 5% H_2-Ar) في المدى الحراري (300–600 م°). الموصلية الأيونية للالكتروليت المتراكب كانت كالتالي $0.12–1.24 \times 10^{-5}$ و $0.13–7.97 \times 10^{-5}$ سمنس/سم في الهواء و الهيدروجين الرطب على التوالي.

الكلمات المفتاحية: السريا المُطّعم بالكالسيوم،تأثير المتراكب، الموصلية الأيونية، الالكتروليت المتراكب النانوي، الكربونان الثلاثية.

1. Introduction

Composite solid electrolytes (CSEs) represent an important class of high ionic conducting electrolyte materials in which the conductivity occurs via interfaces. Basically, composites are mixtures of two or more phases with the combination of different properties such as high conductivity and enhanced mechanical properties (e.g., higher strength) [1, 2]. These properties make them promising candidates as electrolytes for solid state electrochemical devices. In 1973, Liang [3] reported that the Li^+ ionic conductivity of lithium iodide (LiI) increased significantly by the addition of aluminum oxide (Al_2O_3) as second phase. Since then, a large number of composite solid electrolytes have been investigated, in particular dual phase oxide-salt based composite materials such as; oxide-halide (e.g., GDC–$LiCl/SrCl_2$), oxyacid salt-oxide (e.g., Li_2SO_4–Al_2O_3) and oxide-carbonate (e.g., GDC-carbonate) [2, 4-6] etc.

In addition to oxide-salt composite electrolytes, two phase composites based on oxide-oxide electrolyte materials have been investigated as well. Mishima et al. [7] demonstrated a composite electrolyte of two oxide ion conductors in which SDC was dispersed in a matrix of YSZ. In that study it was found that YSZ matrix effectively suppressed the electronic conduction caused by SDC reduction. Recently, Xu et al. [8] synthesised a composite consisting of two oxide ion conductors $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM). It was found that the ionic conductivity of SDC–LSGM composite improved by addition of 10 wt% of LSGM. A composite electrolyte of oxide-oxide system based on the mixture of oxygen ion conductor $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and proton ion conductor $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (SDC–BCY) was first studied by Zhu et al. [9]. Since then several oxide ion/proton ion conductors have been investigated such as $Ce_{0.8}Sm_{0.2}O_{2-\delta}$-$BaCe_{0.8}Sm_{0.2}O_{3-\delta}$ (SDC–BCS) [10],

$Ce_{0.8}Gd_{0.2}O_{2-\delta}$–$BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (GDC–BCY) [11] and $Ce_{0.8}Y_{0.2}O_{2-\delta}$–$BaZ_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (YDC–BZCY), etc. [12]. In addition to the ionic conductivity enhancement, by mixing doped ceria with proton conductor the composites will display dual (O^{2-}/H^{+}) ion conduction simultaneously in H_2/air fuel cell [9].

Among the aforementioned composite electrolytes, doped ceria-carbonate based systems have drown considerable attention in recent years owing to their increasing application as electrolytes for intermediate/low temperature (300–600 °C) solid oxide fuel cells (LT/IT–SOFCs) [13, 14]. Another potential application for these materials include; water (steam) electrolysis [15], electrochemical synthesis of ammonia [16, 17], direct carbon fuel cells (DCFCs), and carbon dioxide (CO_2) permeation membrane [18]. These composite electrolytes consist of doped ceria (e.g. SDC) as a host phase and carbonate (e.g. Na_2CO_3, $(Li/Na)_2CO_3$, $(Li/Na/K)_2CO_3$) as a second phase [13, 14, 19]. These materials exhibit high ionic conductivity (> 0.1 S cm^{-1}) below 600 °C which is higher than that of pure doped ceria (10^{-2} S cm^{-1}) at 600 °C [20]. The conductivity enhancement is related to the fast ionic transport at the interface region between the two phases [21]. Besides to the enhanced ionic conductivity and stability, the addition of carbonate phase is found to suppress the electronic conduction of doped ceria caused by the partial reduction of Ce^{4+} to Ce^{3+} in reducing atmosphere. Furthermore, it was reported that, doped-carbonate composites are co-ionic (O^{2-}/H^{+}) conductors in the presence of oxygen and wet hydrogen-containing atmospheres [13]. In recent years, the concept of ternary ionic conduction $(O^{2-}/H^{+}/CO_3^{2-})$ in ceria-carbonate composite electrolytes has been also proposed [22]. In the present study, Ca-doped ceria-carbonate composite electrolyte has been prepared. The ionic conduction of the composite electrolyte was investigated by employing impedance spectroscopy (IS).

2. Experimental

2.1 Synthesis of $Ce_{0.8}Ca_{0.2}O_{2-\delta}$ powder

Ca-doped ceria (CDC) powder with a composition of ($Ce_{0.8}Ca_{0.2}O_{2-\delta}$) was synthesised via a co-precipitation method as described elsewhere [23]. Cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, Alfa Aesar, 99.5%) and calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$, Alfa Aesar, 99%) were used as starting materials. Calculated amounts of $Ce(NO_3)_3{\cdot}6H_2O$ and $Ca(NO_3)_2{\cdot}4H_2O$ were dissolved in 50 mL of deionised water. An aqueous solution of ammonium oxalate monohydrate ($(NH_4)_2C_2O_4{\cdot}H_2O$, Alfa Aesar, 98+%) with a concentration of 0.3 M was used as the precipitating agent. The mixed salts solution was added at rate of 8 rmp to 150 mL ammonium oxalate solution (0.3 M) under vigorous stirring at room temperature. A white precipitate was formed which was stirred for 1h for homogenisation and then vacuum filtered, washed several times with deionised water and ethanol, and then dried at 80 °C overnight. The obtained powder was calcined in air at 600 °C for 2h with heating/cooling rates of 5 °C min^{-1}. Finally, ultrafine yellow powder of CDC was obtained. A flow chart for the overall experiment is shown in Fig.1.

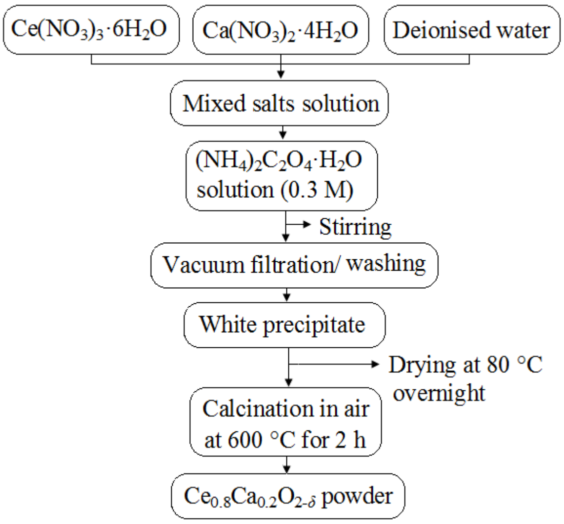

Fig.1 A schematic diagram for preparation of $Ce_{0.8}Ca_{0.2}O_{2-\delta}$.

2.2 Preparation of the composite electrolyte

The ternary eutectic salt ($(Li/Na/K)_2CO_3$) was separately prepared by solid state reaction. Lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3,) were mixed with a molar ratio of 43.5:31.5:25 respectively [24]. The mixture was calcined in air at 600 °C for 1h and quenched directly to room temperature. The composite electrolyte CDC–$(Li/Na/K)_2CO_3$ was prepared by mixing CDC powder with the ternary carbonate salt at weight ratio of 80:20. The mixture was ground thoroughly with an agate mortar and acetone. The material was fired in air at 680 °C for 1h in sequence before being quenched to room temperature [22]. The obtained powder was ground thoroughly for subsequent use.

2.3 Characterisation

2.3.1 X-ray powder diffraction

X-ray diffraction (XRD) data were carried out by a Panalytical X'Pert Pro diffractometer with a Ni-filtered CuKα radiation (λ=1.5405 Å), using 40 kV and 40 mA, fitted with a X'Celerator detector. Absolute scans were recorded in the 2θ range 5–100°. The crystalline sizes of the prepared materials estimated using Debye-Scherrer formula (Equation 1) [25].

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

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

2.3.2 Conductivity

The conductivity measurements were carried out on frequency response analyser 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 at pressure of 4 tons into pellets with diameter of 13 mm and thickness of ~ 2 mm. The green pellets were sintered in air at 700 °C for 2h at rate of 2 °C heating/cooling. 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. AC impedance measurements were carried out in two atmospheres, namely; air and wet 5% H_2–Ar. The measurements were in the temperature range of 300–600 °C. The AC conductivities were calculated using Equation 2 [26].

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

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 powder XRD pattern of the ternary carbonate, pure CDC and CDC–$(Li/Na/K)_2CO_3$ composite electrolytes are shown in Fig.2. As can be seen from Fig.2a, the ternary carbonates which was calcined in air at 600 °C for 1h show a complicated phase composition. A single phase CDC with cubic fluorite structure was obtained after firing the CDC precursor at 600 °C in air for 2h, which is in good agreement with JCPDS file 34-394 as presented in Fig.2b. Fig.2c represents the XRD pattern of CDC–carbonate composite calcined in air at 680 °C for 1h and quenched directly to room temperature. As can be seen the major peaks could be ascribed to the pure CDC phase, whereas very small additional peaks at 32.35°, 34.63°, 37.32° and 53.89° were observed which could be identified as $(Li/Na/K)_2CO_3$. This indicates that the majority of the ternary carbonates in the composite electrolyte present in amorphous phase. The crystallite size of pure CDC is ~ 17.03 nm, while that of CDC-carbonate composite is ~ 33.51 nm, estimated from Sherrer's formula (Equation 1).

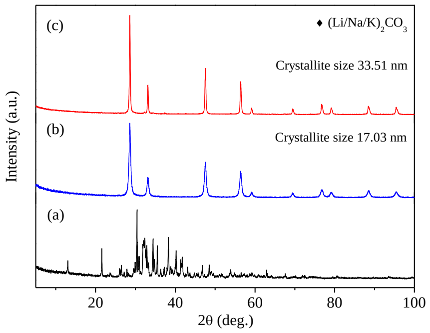

Fig.2 XRD patterns of (a) $(Li/Na/K)_2CO_3$ calcined in air at 600 °C for 1h; (b) CDC calcined at 600 °C for 2h; (c) CDC–$(Li/Na/K)_2CO_3$ composite calcined at 680 °C for 1h.

3.2 The ionic conductivity

The ionic conductivities of the composite electrolyte in two different atmospheres (air and wet 5% H_2–Ar) as function of temperature are shown in Fig.3. As can be seen, the ionic conductivities of the composite electrolyte increase with increasing the operating temperature in both atmospheres under investigations. Under hydrogen gas atmosphere, the proton ion (H^+) conductivity is the main contributor to the overall measured conductivity, while the conductivity measured under air is mainly resulting from oxygen ion (O^{2-}) conductivity. It can be also seen from Fig.3 that, the proton ion conductivity of CDC–$(Li/Na/K)_2CO_3$ nanocomposite electrolyte is higher than the oxygen ion conductivity over the whole temperature range (300-600 °C), which is in good agreement with the conductivity curves of CDC–Na_2CO_3 composite as reported by Ma et al. [23]. In addition, it can be clearly seen that the conductivity changed at two regions below and above ~ 400 °C, which is the melting point of the ternary carbonate ($(Li/Na/K)_2CO_3$) [24]. This conductivity jump phenomenon above the carbonate melting point has also been observed for doped ceria-ternary carbonate composite (SDC–$(Li/Na/K)_2CO_3$) [22], doped ceria-binary carbonate composite (e.g. SDC– or GDC–$(Li/Na)_2CO_3$) [13, 27] and non-ceria-binary carbonate composite (e.g. $LiAlO_2$– or LSGM–$(Li/Na)_2CO_3$) [28, 29].

At high temperature (400–600 °C), the total conductivities of the composite electrolyte (CDC–$(Li/Na/K)_2CO_3$) were found to be 0.12–3.51 × 10^{-3}, and 0.13–2.03 × 10^{-2} S cm^{-1} in air and wet 5% H_2–Ar respectively. These values are higher than those reported by Ma et al. [23] for pure CDC (~ 10^{-3} S cm^{-1}) and for CDC–Na_2CO_3 nanocomposite electrolyte (5.4 × 10^{-3} S cm^{-1}) in air at 600 °C. The apparent activation energies (Ea) of the composite electrolyte at high temperature (600–400 °C) under different atmospheres were extracted from the slope of each series of points in the Arrhenius plots of conductivity as shown in Fig.4. The calculated activation energies were found to be 0.55 ± 0.16 eV and 0.99 ± 0.36 eV for the composite electrolyte in air and wet 5% H_2-Ar respectively.

The enhancement in the ionic conductivities above the melting point of the ternary carbonate could be ascribed to the so-called the composite effect. This could be due to that the ternary carbonate softens or becomes molten at high temperature (400–600 °C), which enhances the mobility of all ions (i.e. Li^+, Na^+, K^+, O^{2-}, H^+, HCO_3^-, and CO_3^{2-}) leading to a superionic conducting region at the interface between the two phases. Thus, all these mobile ions contribute to the overall measured ionic conductivity [28].

At low temperature (300–350 °C), the ionic conductivities of the composite electrolyte dropped significantly (Fig.3.) and were found to be 6.34 × 10^{-4}–1.24 × 10^{-5} in air and 3.42 × 10^{-3}–7.97 × 10^{-5} S cm^{-1} in wet 5% H_2-Ar. Below the carbonate melting point, the ions are not highly activated and less mobile, due to the activation barrier, leading to low ionic conductivities within this temperature range [30]. However, the proton ion conductivity of the composite electrolyte is still higher than the oxygen ion conductivity, as seen from Fig.3. This could be due to the fact that proton conduction can be easily activated at low temperature, compared to oxygen-ion conduction [15, 31].

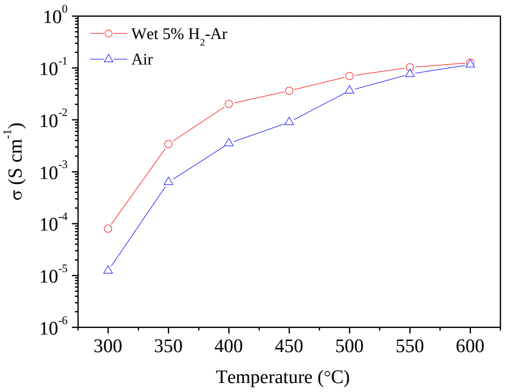

Fig.3 AC ionic conductivity plot against temperature for CDC–$(Li/Na/K)_2CO_3$ composite in air and wet 5% H_2–Ar atmospheres.

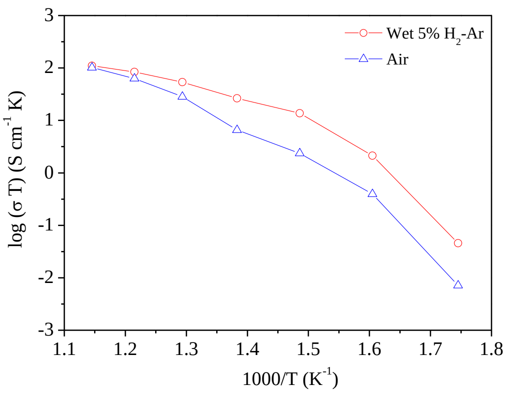

Fig.4 Arrhenius plot of the total conductivity for CDC–$(Li/Na/K)_2CO_3$ composite in air and wet 5% H_2–Ar atmospheres.

Figs.5a and b respectively show the XRD patterns of the CDC–carbonate composite electrolyte before and after the 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 CDC–$(Li/Na/K)_2CO_3$ composite electrolyte.

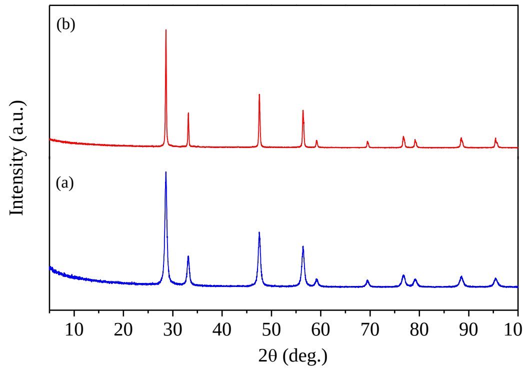

Fig.5 XRD patterns of CDC–$(Li/Na/K)_2CO_3$: (a) before conductivity measurement; (b) after conductivity measurement.

4. Conclusion

Ca-doped ceria (CDC) powder with a composition of ($Ce_{0.8}Ca_{0.2}O_{2-\delta}$) was synthesised via a co-precipitation method using an ammonium oxalate as a precipitating agent. A new composite electrolyte was prepared by mixing $Ce_{0.8}Ca_{0.2}O_{2-\delta}$ with the ternary carbonate ($(Li/Na/K)_2CO_3$) at the ratio of 80:20 respectively. The phase composition of the prepared materials was characterised by X-ray diffraction (XRD). The XRD results demonstrated that a single phase CDC with cubic fluorite structure was obtained and the CDC phase structure did not change by introducing the ternary carbonates as a second phase. The ionic conductivity of the composite electrolyte was found to be $0.12-1.24 \times 10^{-5}$, and $0.13-7.97 \times 10^{-5}$ S cm^{-1} in air and wet 5% H_2–Ar respectively. After the conductivity measurements, the composite electrolyte retained its fluorite structure, indicating its stability on both oxidising and reducing atmospheres.

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