# Ionic Conduction in Ceria/sodium Carbonate Nano Composite Based Electrolyte

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## Abstract

Composite solid electrolytes (CSEs) are heterogeneous mixtures of at least two solid materials which exhibit high ionic conductivities, high stabilities (thermal and chemical) and enhanced mechanical strength [1, 2]. These unique properties make them suitable electrolyte materials for many solid-state electrochemical cells. In 1973, Liang [3] reported a remarkable enhancement of lithium iodide (LiI) ionic conductivity after adding a second phase of aluminium oxide ($Al_2O_3$). Since then, the ionic conductivities of many composite electrolytes including; halide/oxide, oxyacid salt/oxide and carbonate/oxide have been investigated.

In recent years, ceria-based nanocomposites, in particular ceria-carbonate, have attracted more attention owing to their super-ionic conductivities (0.1 >S $cm^{-1}$at above 300 °C), negligible electronic conduction, multi-ionic conduction ($O^{2-}$, $H^+$,$CO_3^{2-}$), fast ionic transport and thermodynamic stability[4-6].These nanocomposite electrolytes composed of ceria (e.g., $Ce_{0.8}Sm_{0.2}O_{2-\delta}$, $Ce_{0.8}Sm_{0.18}Ca_{0.02}O_{2-\delta}$) as a host phase and carbonate (e.g., $Na_2CO_3$, $(Li/Na)_2CO_3$, $(Li/Na/K)_2CO_3$) as a second phase.Besides, the addition of carbonate not only enhances the ionic conductivities of the composite electrolytes but also suppers the electronic conduction in the ceria ($CeO_2$) phase due to the reduction of $Ce^{4+}$ to $Ce^{3+}$ in hydrogen-containing atmospheres.

Ceria/carbonate-based composites, owing their aforementioned properties, have been explored as electrolytes for many applications including; solid oxide fuel cells (SOFCs)[7, 8], carbon dioxide ($CO_2$) permeation membrane[9], direct carbon fuel cells (DCFCs) [10], water (steam) electrolysis [11] and electrochemical synthesis of ammonia [12].

In most of the above-mentioned studies, the composite electrolytes are consist of singly or co-doped ceria and carbonate (single, binary or ternary). In our previous study, the ionic conductivities of pure ceria/ternary carbonate ($CeO_2/(Li/Na/K)_2CO_3$) were investigated. In the air, the AC total ionic conductivities were $3.45 \times 10^{-2}$ and 0.248 S $cm^{-1}$ at 400-600 ºC, respectively. In 5% $H_2$-Ar the ionic conductivities were about $5.33 \times 10^{-2}$ to 0.231 S $cm^{-1}$ at 400-600 ºC, respectively[13].In another study, Ristoiu et al. [14]have prepared a composite electrolyte based on pure ceria (i.e., un-doped) and single carbonate ($Na_2CO_3$) aiming to eliminate the effect of both ceria dopants and eutectic carbonate mixture. The DC ionic conductivity of $CeO_2/Na_2CO_3$ was approximately $7.3 \times 10^{-4}$ S $cm^{-2}$in the air at 600 ºC.

This study aims to explore the AC ionic conductivities ($O^{2-}$conductivity) of $CeO_2/Na_2CO_3$ in air and 5% $H_2$-Ar ($H^+$conductivity) at 400 to 640 C. The composite electrolyte was prepared by mixing a commercially available cerium oxide ($CeO_2$) and sodium carbonate ($Na_2CO_3$) in a weight ratio of 80:20 wt%. The mixture was fired in the air at 680 °C for 1 h. The composite electrolyte was investigated using X-ray powder diffraction (Figure 1).

As shown in the X-ray patterns, the composite electrolyte (Figure 1b) exhibited only the peaks that belong to pure ceria phase (Figure 1a). Besides, the crystallite size of $CeO_2$ was estimated to be 97.01nm whereas that of $CeO_2/Na_2CO_3$ composite was about 72.11 nm. After obtaining the composite electrolyte of interest, its corresponding powder was pressed into 13 mm diameter pellet (~ 2 mm in thickness) before being sintered in air at 700 °Cfor 1 h, as schematically represented in Figure 2.

Afterwards, the sintered pellet was coated on both sides by silver paste and fired at 550 °C to form porous electrodes. Then, the pellet was placed in the AC conductivity measurement jig (Figure 3). The ionic conductivities measurements were performed using pseudo 4-probe AC impedance spectroscopy under air and wet (~ 3% $H_2O$) 5% $H_2$-Ar in the range of temperature 400-650 °C. Figure 4 shows the AC ionic conductivities of $CeO_2/Na_2CO_3$ composite electrolyte in air and wet 5% $H_2$-Ar as a function of measuring temperature.

As shown, the ionic conductivities in both atmospheres increased gradually with increasing the measuring temperature from 400 to 650 °C. In the air, the total ionic conductivities werefound to be $1.23 \times 10^{-2}$and $8.71 \times 10^{-2}$ S $cm^{-1}$ at 400 to 650 °C, respectively.

In the case of wet 5% $H_2$-Ar atmosphere, total ionic conductivities were approximately $1.92 \times 10^{-2}$ and $9.96 \times 10^{-2}$ S $cm^{-1}$ at 400 to 650 °C, respectively.However, the ionic conductivities of the composite electrolyte in wet 5% $H_2$-Ar which represent the proton ionic conduction($H^+$) were higher than those obtained in the air (i.e., oxygen-ion conduction, $O^{2-}$) in all range of measuring temperature. This indicates that the proton ion conduction is dominant in $CeO_2/Na_2CO_3$ nanocomposite electrolytewithin the range of measured temperature (400 to 650 °C).

The activation energy ($E_a$) of the composite electrolyte in air and wet 5% $H_2$-Ar, estimated from Arrhenius plot (Figure 4), were found to be 0.48 ±0.15 and 0.42 ±0.06, respectively. The obtained results suggest that $CeO_2/Na_2CO_3$ can be considered as promising electrolyte materials for either protonic and oxygen-ion conducting based electrolytic cells.

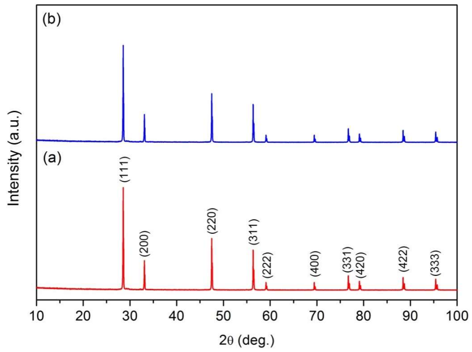

**Figure 1.**XRD patterns of; (a) commercial $CeO_2$, (b) $CeO_2/Na_2CO_3$ nanocomposite electrolyte calcined in air at 680 ºC for 1 h

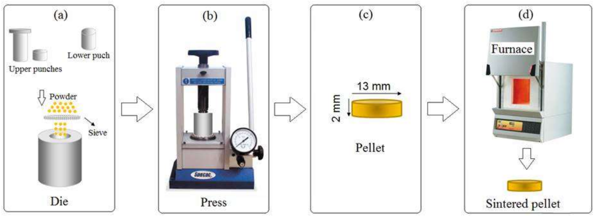

**Figure 2.**Schematic representation of pellets preparation and sintering. (a) die filling; (b) powder pressing; (c) green pellet; (d) pellet sintering

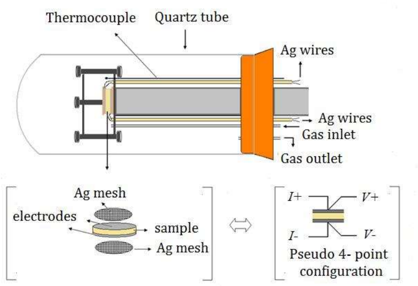

**Figure 3.**Schematic representation for experimental set up for AC conductivity measurement[15]

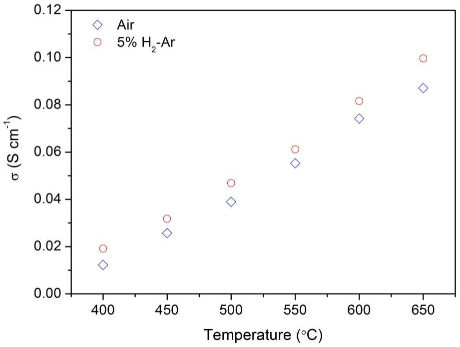

**Figure 4.**AC ionic conductivity plot of $CeO_2$-$Na_2CO_3$ nanocomposite electrolyte under air and 5% $H_2$-Ar atmospheres

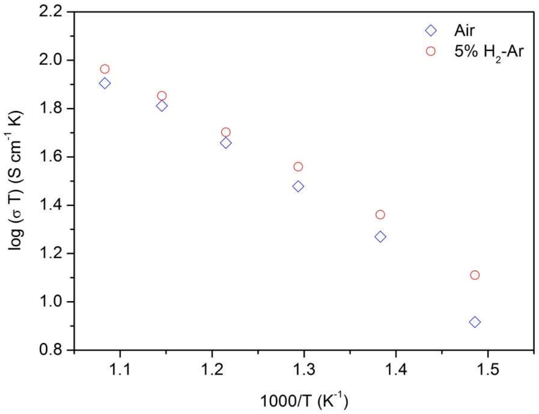

**Figure 5.**Arrhenius plots of the total AC ionic conductivities of $CeO_2$-$Na_2CO_3$ nanocomposite electrolyte in air and wet 5% $H_2$-Ar

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