

# 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 ( $\text{Al}_2\text{O}_3$ ). 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 ( $0.1 > \text{S cm}^{-1}$  at above  $300^\circ\text{C}$ ), negligible electronic conduction, multi-ionic conduction ( $\text{O}^{2-}$ ,  $\text{H}^+$ ,  $\text{CO}_3^{2-}$ ), fast ionic transport and thermodynamic stability [4-6]. These nanocomposite electrolytes composed of ceria (e.g.,  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ ,  $\text{Ce}_{0.8}\text{Sm}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$ ) as a host phase and carbonate (e.g.,  $\text{Na}_2\text{CO}_3$ ,  $(\text{Li}/\text{Na})_2\text{CO}_3$ ,  $(\text{Li}/\text{Na}/\text{K})_2\text{CO}_3$ ) as a second phase. Besides, the addition of carbonate not only enhances the ionic conductivities of the composite electrolytes but also suppresses the electronic conduction in the ceria ( $\text{CeO}_2$ ) phase due to the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  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 ( $\text{CO}_2$ ) 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 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 ( $\text{CeO}_2/(\text{Li}/\text{Na}/\text{K})_2\text{CO}_3$ ) were investigated. In the air, the AC total ionic conductivities were  $3.45 \times 10^{-2}$  and  $0.248 \text{ S cm}^{-1}$  at  $400$ - $600^\circ\text{C}$ , respectively. In  $5\% \text{ H}_2\text{-Ar}$  the ionic conductivities were about  $5.33 \times 10^{-2}$  to  $0.231 \text{ S cm}^{-1}$  at  $400$ - $600^\circ\text{C}$ , 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 ( $\text{Na}_2\text{CO}_3$ ) aiming to eliminate the effect of both ceria dopants and eutectic carbonate mixture. The DC ionic conductivity of  $\text{CeO}_2/\text{Na}_2\text{CO}_3$  was approximately  $7.3 \times 10^{-4} \text{ S cm}^{-2}$  in the air at  $600^\circ\text{C}$ .

This study aims to explore the AC ionic conductivities ( $\text{O}^{2-}$  conductivity) of  $\text{CeO}_2/\text{Na}_2\text{CO}_3$  in air and  $5\% \text{ H}_2\text{-Ar}$  ( $\text{H}^+$  conductivity) at  $400$  to  $640^\circ\text{C}$ . The composite electrolyte was prepared by mixing a commercially available cerium oxide ( $\text{CeO}_2$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in a weight ratio of  $80:20 \text{ wt\%}$ . The mixture was fired in the air at  $680^\circ\text{C}$  for  $1 \text{ h}$ . 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  $\text{CeO}_2$  was estimated to be  $97.01 \text{ nm}$  whereas that of  $\text{CeO}_2/\text{Na}_2\text{CO}_3$  composite was about  $72.11$

$\text{nm}$ . After obtaining the composite electrolyte of interest, its corresponding powder was pressed into  $13 \text{ mm}$  diameter pellet ( $\sim 2 \text{ mm}$  in thickness) before being sintered in air at  $700^\circ\text{C}$  for  $1 \text{ h}$ , as schematically represented in Figure 2. Afterwards, the sintered pellet was coated on both sides by silver paste and fired at  $550^\circ\text{C}$  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 ( $\sim 3\% \text{ H}_2\text{O}$ )  $5\% \text{ H}_2\text{-Ar}$  in the range of temperature  $400$ - $650^\circ\text{C}$ . Figure 4 shows the AC ionic conductivities of  $\text{CeO}_2/\text{Na}_2\text{CO}_3$  composite electrolyte in air and wet  $5\% \text{ H}_2\text{-Ar}$  as a function of measuring temperature. As shown, the ionic conductivities in both atmospheres increased gradually with increasing the measuring temperature from  $400$  to  $650^\circ\text{C}$ . In the air, the total ionic conductivities were found to be  $1.23 \times 10^{-2}$  and  $8.71 \times 10^{-2} \text{ S cm}^{-1}$  at  $400$  to  $650^\circ\text{C}$ , respectively. In the case of wet  $5\% \text{ H}_2\text{-Ar}$  atmosphere, total ionic conductivities were approximately  $1.92 \times 10^{-2}$  and  $9.96 \times 10^{-2} \text{ S cm}^{-1}$  at  $400$  to  $650^\circ\text{C}$ , respectively. However, the ionic conductivities of the composite electrolyte in wet  $5\% \text{ H}_2\text{-Ar}$  which represent the proton ionic conduction ( $\text{H}^+$ ) were higher than those obtained in the air (i.e., oxygen-ion conduction,  $\text{O}^{2-}$ ) in all range of measuring temperature. This indicates that the proton ion conduction is dominant in  $\text{CeO}_2/\text{Na}_2\text{CO}_3$  nanocomposite electrolyte within the range of measured temperature ( $400$  to  $650^\circ\text{C}$ ). The activation energy ( $E_a$ ) of the composite electrolyte in air and wet  $5\% \text{ H}_2\text{-Ar}$ , estimated from Arrhenius plot (Figure 4), were found to be  $0.48 \pm 0.15$  and  $0.42 \pm 0.06$ , respectively. The obtained results suggest that  $\text{CeO}_2/\text{Na}_2\text{CO}_3$  can be considered as promising electrolyte materials for either protonic and oxygen-ion conducting based electrolytic cells.

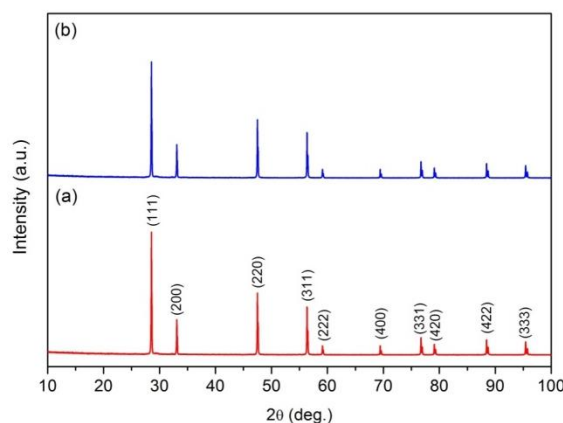


Figure 1. XRD patterns of; (a) commercial  $\text{CeO}_2$ , (b)  $\text{CeO}_2/\text{Na}_2\text{CO}_3$  nanocomposite electrolyte calcined in air at  $680^\circ\text{C}$  for  $1 \text{ h}$

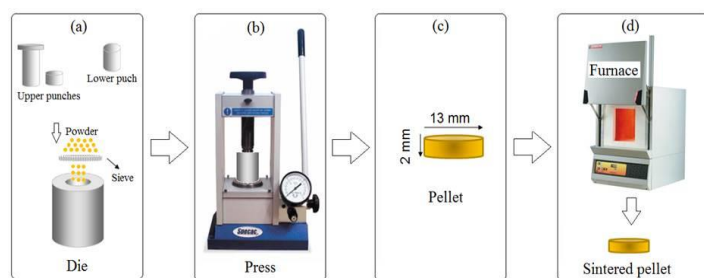


Figure 2. Schematic representation of pellets preparation and sintering. (a) die filling; (b) powder pressing; (c) green pellet; (d) pellet sintering

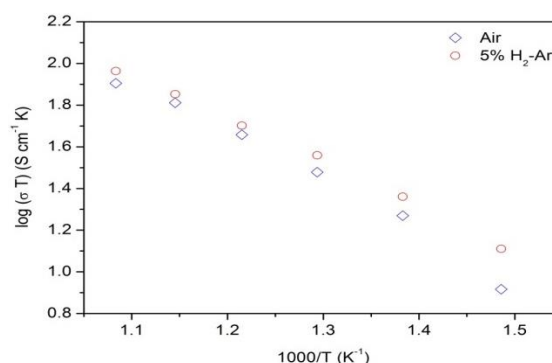


Figure 5. Arrhenius plots of the total AC ionic conductivities of CeO<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub> nanocomposite electrolyte in air and wet 5% H<sub>2</sub>-Ar

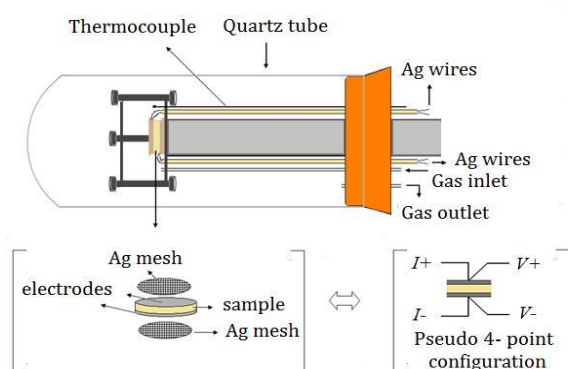


Figure 3. Schematic representation for experimental set up for AC conductivity measurement [15]

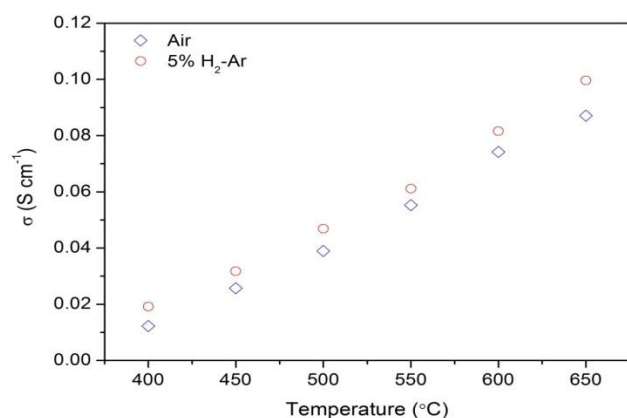


Figure 4. AC ionic conductivity plot of CeO<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub> nanocomposite electrolyte under air and 5% H<sub>2</sub>-Ar atmospheres

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