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 (Al₂O₃). 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, fast ionic transport and thermodynamic stability[4-6]. These nanocomposite electrolytes composed of ceria (e.g., Ce₀.₈Sm₀.₂O₁.₅, Ce₀.₈Sm₀.₁₈Ca₀.₀₂O₁.₅) as a host phase and carbonate (e.g., Na₂CO₃, (Li/Na)₂CO₃, (Li/Na/K)₂CO₃) 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 (CeO₂) phase due to the reduction of Ce⁴⁺ to Ce³⁺ 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 (CO₂) 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 (CeO₂/(Li/Na/K)₂CO₃) were investigated. In the air, the AC total ionic conductivities were 3.45 × 10⁻² and 0.248 S cm⁻¹ at 400-600 °C, respectively. In 5% H₂-Ar the ionic conductivities were about 5.33 × 10⁻² to 0.231 S cm⁻¹ at 400-600 °C, respectively[13]. In another study, Ristoiu et al. [14] have prepared a composite electrolyte based on pure ceria (i.e., undoped) and single carbonate (Na₂CO₃) aiming to eliminate the effect of both ceria dopants and eutectic carbonate mixture. The DC ionic conductivity of CeO₂/Na₂CO₃ was approximately 7.3 × 10⁻⁴ S cm⁻¹ in the air at 600 °C.

This study aims to explore the AC ionic conductivities (O²⁻ conductivity) of CeO₂/Na₂CO₃ in air and 5% H₂-Ar (H⁺ conductivity) at 400 to 640 °C. The composite electrolyte was prepared by mixing a commercially available cerium oxide (CeO₂) and sodium carbonate (Na₂CO₃) 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 CeO₂ was estimated to be 97.01 nm whereas that of CeO₂/Na₂CO₃ 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 °C for 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% H₂O) 5% H₂-Ar in the range of temperature 400-650 °C. Figure 4 shows the AC ionic conductivities of CeO₂/Na₂CO₃ composite electrolyte in air and wet 5% H₂-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 were found to be 1.23 × 10⁻² and 8.71 × 10⁻² S cm⁻¹ at 400 to 650 °C, respectively.

In the case of wet 5% H₂-Ar atmosphere, total ionic conductivities were approximately 1.92 × 10⁻² and 9.96 × 10⁻² S cm⁻¹ at 400 to 650 °C, respectively. However, the ionic conductivities of the composite electrolyte in wet 5% H₂-Ar which represent the proton ionic conduction(H⁺) were higher than those obtained in the air (i.e., oxygen-ion conduction, O²⁻) in all range of measuring temperature. This indicates that the proton ion conduction is dominant in CeO₂/Na₂CO₃ nanocomposite electrolyte within the range of measured temperature (400 to 650 °C).

The activation energy (E_a) of the composite electrolyte in air and wet 5% H₂-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 CeO₂/Na₂CO₃ 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$_2$CO$_3$ 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$_2$CO$_3$ nanocomposite electrolyte under air and 5% H$_2$-Ar atmospheres

Figure 5. Arrhenius plots of the total AC ionic conductivities of CeO$_2$-Na$_2$CO$_3$ nanocomposite electrolyte in air and wet 5% H$_2$-Ar

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