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) above 300 °C, negligible electronic conduction, multi-ionic conduction (O2−, H+, CO32−), fast ionic transport and thermodynamic stability [4-6]. These nanocomposite electrolytes composed of ceria (e.g., CeO2−xSm2O3−y), CeO2−xNa2O+y or CeO2−xCO2−y as a host phase and carbonate (e.g., Na2CO3, Li2Na4CO3, (Li/Na)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/Na2O/K2CO3) 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., un-doped) 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−xNa2CO3 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−xNa2CO3 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 × 10−3 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 × 10−3 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−xNa2CO3 nanocomposite electrolyte within the range of measured temperature (400 to 650 °C). The activation energy (Ea) 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−xNa2CO3 can be considered as promising electrolyte materials for either protonic and oxygen-ion conducting based electrolytic cells.

Figure 1.XRD patterns of; (a) commercial CeO2, (b) CeO2/Na2CO3 nanocomposite electrolyte calcined in air at 680 °C for 1 h.
EXTENDED ABSTRACT

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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