



Electrochemical properties of dual phase neodymium-doped ceria alkali carbonate composite electrolytes in intermediate temperature



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HIGHLIGHTS

- Understand the behaviors of multi-ionic conduction of ceria/carbonate electrolyte.
- Conductivities of NDC and NDC/carbonate are investigated as a function of a_{O_2} and a_{H_2O} .
- Transference numbers are measured by the oxygen- and hydrogen-concentration cells.
- Dominant charge carriers are identified by the analysis of partial conductivity.

ARTICLE INFO

Article history:

Received 1 September 2014

Received in revised form

17 October 2014

Accepted 26 October 2014

Available online 28 October 2014

Keywords:

Dual-phase electrolytes

Transference number

Electrical conductivity

Concentration cell

Multi-ion conduction

ABSTRACT

Composite electrolyte materials composed of neodymium-doped ceria ($Nd_{0.2}Ce_{0.8}O_{1.9}$; NDC) and $(Li-0.5Na)_2CO_3$ are investigated to understand the unique behaviors of their multi-ionic conduction. In the intermediate temperature, the NDC-based carbonate composite electrolytes exhibit a much higher conductivity compared to pure NDC. It has been claimed that the oxide ions are transported in the doped-ceria phase via oxygen vacancies and the protons are conducted through the second carbonate phase, thereby resulting in an enhanced ionic conductivity. However, it has not been experimentally demonstrated if the proton conduction within the carbonate phase aided in improving the conductivity of oxygen ions in the composite system. Hence, the primary objective of this work is to cultivate a deeper insight into the conduction property of these composites as an attempt to clarify the ionic transport phenomenon responsible for enhanced conductivity. Electrical conductivities of NDC and NDC/carbonate materials are investigated as a function of oxygen partial pressure and vapor pressure of water to understand transport properties of composite electrolytes. The ionic and electronic transference numbers of composite electrolytes are measured by the oxygen- and hydrogen-concentration cells containing water. The dominant charge carriers are identified quantitatively through the analysis of the partial conductivity of proton, oxygen ions, and electrons (holes). Understanding the transport properties and transference numbers of composite electrolytes can contribute to the development of commercial solid oxide fuel cells, which can be done by reducing the operating temperature using a highly ionic conductive NDC/carbonate composite electrolyte at the intermediate temperature.

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1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that convert fuel to electricity, which have various advantages as alternative power sources, such as outstanding fuel flexibility, high-

energy conversion efficiency, and environmental friendly [1–3]. Despite their various merits, conventional SOFCs with typical yttria-stabilized zirconia (YSZ) electrolytes require high operation temperature (>800 °C) to obtain sufficient oxygen-ion conductivity [4]. The higher temperature accelerates the degradations of cell components, increases manufacturing costs, and complicates the design and choice of balance-of-plant (BOP) components. Therefore, in order to develop commercial SOFCs, reducing the operating

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temperature through the use of a highly ionic conductive electrolyte at the intermediate temperature (IT; <700 °C) is one of the key issues [5–7]. There are many research and development (R&D) works on the development of IT-SOFCs with a new generation of electrolytes. The most interesting IT oxygen-ion conducting electrolytes are the ceria-based electrolytes, such as samarium-doped ceria (SDC), gadolinium-doped ceria (GDC) and neodymium-doped ceria (NDC). Among these doped-ceria systems, NDC electrolytes exhibited the highest ionic conductivities at the IT [7–9]. However, ceria-based electrolytes are of limited use because of their ceria reduction in reducing atmosphere (low oxygen partial pressure). Therefore, developing advanced electrolytes with a high ion conductivity and stability is still one of the chief objectives.

In the last decade, ceria-based carbonate composite electrolytes comprising of a doped ceria (host phase, such as NDC or SDC) and alkali carbonate salts (second phase, such as Li_2CO_3 – K_2CO_3 or Li_2CO_3 – Na_2CO_3) have been developed as electrolytes for IT-SOFCs [10–17]. These materials have a higher ionic conductivity than those of pure ceria-based electrolytes with a conductivity of 0.1 S cm^{-1} at <600 °C, when approaching the carbonates melting temperature. The ceria/carbonate interface might play a role in the charge-transport process with the coexistence of several charge carriers (CO_3^{2-} , O^{2-} and H^+). In particular, it has been noted that the oxide ions are transported in the doped-ceria phase via oxygen vacancies, while the protons are conducted through the second-carbonate phase. This dual H^+/O^{2-} conduction greatly improve the electrical conductivity of electrolytes, which results in excellent IT-SOFC performances. For example, Raza et al. [18] showed that the use of Na_2CO_3 as the carbonate phase achieved a 1.15 W cm^{-2} at 500 °C. Similarly, a high-power output (1.7 W cm^{-2} at 650 °C) was also obtained with a cell that included the SDC/Li–Na composite by Xia et al. [19].

A detailed review of the conduction mechanism for the ionic conductivity improvement on the ceria-based carbonate composite electrolytes from various points of views of fabrication technologies, carbonate composition, and microstructure have been undertaken in recently published papers [20]. These recent studies have suggested that essentially the interface phase between amorphous carbonate and crystal doped-ceria is to supply the high-speed way for conduction of proton and oxygen ions with the space charge model. Based on the interfacial conduction path using theoretical calculations with the Coulombic model, Zhu et al. [21] predicted that the migration activation energy of the oxygen ionic conduction was 0.2 eV and 1.0 eV for bulk mechanism. A “Swing Model” was also proposed by Wang et al. [22] as a possible mechanism of enhanced ionic conduction in ceria-based carbonate composite electrolytes. They proposed that the significant proton conduction may be achieved in the carbonate via temporal hydrogen bonding. Although plausible explanations with various theoretical models have been presented for interfacial ionic conduction relative to the ceria-carbonate electrolyte, understanding the electrical behavior of such a dual-phase composite is still difficult and unclear. Moreover, it is still unsure if the proton conduction within the carbonate phase does contribute to the improvement of the conductivity of oxygen ions in the ceria-based carbonate composite systems. Therefore, the primary focus of this work is to derive a deeper insight into the conduction behavior of these composites in the attempt to elucidate the ionic transport phenomenon responsible for enhanced conductivity.

Upon exposure to hydrogen, oxygen, and/or water vapor partial-pressure gradient, the concurrent transport of both ionic and electronic charge carriers is forced across a mixed ionic–electronic conducting membrane. In oxygen- or hydrogen-concentration cells, the oxygen ion or proton transference number can be determined under some circumstances only when one gas specie transports

through the composite electrolyte [23,24]. As an example, the oxygen-ion conduction can be taken into consideration because the ceria-based materials are primarily oxygen-ion conductors in an oxygen-containing atmosphere without water, i.e., it is reasonable to neglect the proton and electron transport of ceria-based electrolytes in the same conditions. Conversely, in a hydrogen gas mixture with water, the proton and/or electron transport in ceria/carbonate composites may be taken into consideration as conduction species because ceria-based electrolytes change the mixed ionic–electronic conductor [25]. Furthermore, Wang et al. [22] speculated that the hydrogen bond formed between the $\text{Ce}-\text{O}\cdots\text{H}\text{ctdot};\text{O}-\text{CO}_2^-$ is believed to speed up proton transport. In addition, water vapor may also contribute to the ion (oxygen and/or proton) conduction. In this study, the transport properties of ceria/carbonate composites are analyzed by open-circuit voltage (OCV) measurements on a concentration of oxygen and hydrogen cells with water vapor, which is very effective to quantitatively analyze the contribution of different charge carriers (e.g., H^+ , O^{2-} , e^- and h^+). Based on the in-situ measurements of the ionic and electronic transport properties in a fuel-cell experiment, possible conduction mechanisms are also discussed.

2. Experimental

2.1. Synthesis of the ceria-based composite electrolytes

$\text{Nd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (NDC) powders were synthesized using combustion method of dissolving $\text{Ce}(\text{NO}_3)_3$ (99.99% purity, Kanto Chemical, Japan), $\text{Nd}(\text{NO}_3)_3$ (99.9% purity, Alfa Aesar) and glycine (99.5% purity, Alfa Aesar) into deionized water, and heating the solution on a hot-plate under a magnetic stirrer. NDC precursors obtained by the combustion method were calcined at 400 °C in air for 2 h. Then, the calcined powder was grounded in a mortar and a pestle. For the synthesis of NDC/carbonate composites, the calcined NDC powders were mixed with $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ (2:1 mol%) using zirconia balls in ethanol solvent for 24 h and subsequently dried in the oven to evaporate the ethanol. A mixture of NDC and $(\text{Li}-0.5\text{Na})_2\text{CO}_3$ (25 wt.%) was then pressed uniaxially under 10 MPa. The uniaxially pressed green bodies were then isostatically pressed by the cold-isostatic pressing (CIP) under 200 MPa to improve the density of the composite electrolytes. The resulting pellets were sintered in a furnace of 670 °C for 4 h at a rate of $5 \text{ }^\circ\text{C min}^{-1}$. Gold wires were attached to the gold paste as a current collector for the electrical measurements on both surfaces of the pellet at 650 °C for 1 h.

2.2. Characterizations of composite electrolytes

The crystalline phases of the sintered samples were characterized by X-ray diffraction (XRD, D/MAX 2500, Rigaku, USA) using $\text{Cu-K}\alpha$ radiation in the 2θ range varying from 20° to 80° with a step size of 0.008°. A field-emission-scanning electron microscopy (FE-SEM, S-4700, Hitachi High tech, Japan), and high-resolution transmission electron microscopy (HR-TEM, Titan, FEI, USA) were used to identify the morphology, microstructure, and constituent of NDC/ $(\text{Li}-0.5\text{Na})_2\text{CO}_3$ composite samples. HR-TEM specimens were prepared by dual-beam focused ion beam (FIB) techniques (Helios 600, FEI, USA). The electrical conductivities of the electrolytes were measured using an electrochemical impedance spectroscopy (EIS) instrument with Potentiostat/Galvanostat (SP150, BioLogic, Claix, France) at the temperature range of 250–650 °C at regular intervals of 50 °C. The EIS measurements were carried out in the frequency range of 500 kHz–20 MHz under dry and humidified atmospheres and a reducing gas mixture of 5 vol.% H_2 + 95 vol.% Ar, respectively (humidified via water bubbler at a room temperature). The signal amplitude was 10 mV under OCV conditions.

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