



Solid oxide-molten carbonate nano-composite fuel cells: Particle size effect



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H I G H L I G H T S

- The amount of interface area influences conductivity of the composite strongly.
- In the composite electrolyte, the oxide surface acted as dissociating agent.
- The “liberated” ions at the interface around the oxide particles are more mobile.
- High mobility liberated ions give rise to high ionic conductivity.

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Varying the amount of specific interface area in the $\text{CeO}_2\text{--Na}_2\text{CO}_3$ nanocomposite fuel cell electrolyte helped reveal the role of interfaces in ionic conductivity. We mixed ceria particles with micrometer or nanometer size distributions to obtain a specific surface area (SSA) in the composite from $47 \text{ m}^2 \text{ g}^{-1}$ to $203 \text{ m}^2 \text{ g}^{-1}$. Microstructural investigations of the nanocomposite showed that the Na_2CO_3 phase serves as the glue in the microstructure, while thermal analysis revealed a glass transition-like behavior at $350 \text{ }^\circ\text{C}$. High SSA enhanced the ionic conductivity significantly at temperatures below $400 \text{ }^\circ\text{C}$. Moreover, the activation energy for the Arrhenius conductivity (σT) of the composites was lower than that of the Na_2CO_3 phase. This difference in the activation energies is consistent with the calculated dissociation energy of the carbonate phase. The strong dependence of conductivity on the SSA, along with differences in the activation energies, suggests that the oxide surface acted as a dissociation agent for the carbonate phase. A model for the solid composite electrolyte is proposed: in the nanocomposite electrolyte, the oxide surface helps Na_2CO_3 dissociate, so that the “liberated” ions can move easily in the interaction region around the oxide particles, giving rise to high ionic conductivities.

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1. Introduction

Solid oxide fuel cells (SOFC), are regarded as an attractive alternative energy conversion system for electricity. However, a major drawback limiting a widespread commercialization of such systems was the high operating temperatures near $1000 \text{ }^\circ\text{C}$ of the current zirconia-based SOFC. Efforts to develop electrolyte and electrode materials based on doped ceria have been focused on reducing fuel cell operating temperature to an intermediate temperature range of $300\text{--}500 \text{ }^\circ\text{C}$ [1]. As such, ceria-based ceramics

doped with various rare-earth elements are among the most promising candidates to become an intermediate temperature SOFC (IT-SOFC) electrolyte [2]. The ionic conductivity of doped ceria surpasses corresponding values of yttria-stabilized zirconia (YSZ) at the same temperature by up to 5–100 times [3]. However, an obstacle to the commercialization of ceria-based electrolytes is the reduction of ceria under an H_2 atmosphere. This reduction gives rise to electronic conductivity in the ionic conductor, thereby deteriorating the cell output voltage [4]. One solution proposed used a nano-composite electrolyte, composed of a carbonate and a ceria-based solid oxide [5–12]. In general, the so-called nano-composite electrolytes are composed of doped ceria particles embedded in alkali salts (carbonate, chloride, hydrate, or sulphate) [9,12,13]. The existing knowledge in the scientific literature presumes that oxide particles provide scaffolding for containing the

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carbonate phase at the operating temperatures (400 °C–650 °C). Furthermore, it is assumed that such nano-composite electrolytes remain as two stable phases under the optimized operating conditions [13]. Impressively, this type of composite electrolyte has achieved a conductivity of 0.1 S cm^{-1} at 600 °C, attributed to the transport of H^+ ions and O^{2-} ions [13]. Because of these remarkable characteristics, one leading candidate electrolyte for a new generation of fuel cells is doped ceria nano-composites. Tang et al. investigated the morphological and electrical properties of composites with particle sizes varying from the micrometer to the nano-meter size scale. They found that nano-composite have significantly lower impedance values compared to the micron-sized composite [14]. In theoretical studies, Liu et al. have proposed that the interface layers between SDC and Na_2CO_3 matrix are the origin of the enhanced conductivity [15]. According to their findings, the interfaces would allow a “dual” conduction mechanism through the composite, via H^+ and O^{2-} transport. Furthermore, the pathways for H^+ ions were suggested to exist *along the interface between the component phases* [15]. The O^{2-} transport was assumed to occur through the interconnected SDC phase. According to theoretical calculations, conductivity of the composite electrolyte depended on the volume ratio of SDC to Na_2CO_3 . Another study suggested that H^+ transport occurring along the “implied” interface dominated ionic conduction inside the electrolyte in the temperature range between 300 °C and 600 °C [16]. A conductivity of 0.1 S cm^{-1} was reported for a 20 wt% SDC- Na_2CO_3 nano-composite electrolyte at 300 °C [18]. This was the optimum carbonate amount in the composite according to Zhu et al. [18]. It was argued that conductivity resulted neither from the SDC nor from the Na_2CO_3 phase, as individual SDC and Na_2CO_3 phases are good electrical insulators at $\sim 300 \text{ °C}$ [17]. No other phase was detected in the composite. Hence the interface formed by the two phases was proposed to serve as a new conduction pathway for the nano-composite, offering on one hand a high-conductivity pathway for ionic conduction, and on the other hand, a presumed capacity to increase mobile ion concentration beyond that of the bulk [18]. No atomistic mechanisms have yet been suggested for either phenomenon.

Furthermore, Wang et al. claimed that the high conductivity of the nano-composite electrolyte was attributed to interfacial oxygen ion conduction rather than to bulk oxygen ion conduction [18]. The conduction through the interface was claimed to require low activation energy for O^{2-} transport. No explanation was given for the assumed low activation energy for the oxygen ion transport. The conductivity of the pure Na_2CO_3 is on the order of 10^{-5} – $10^{-4} \text{ S cm}^{-1}$ at the temperature range from 500 °C to 580 °C [15]. This value is much lower than the values reported for the nano-composite electrolyte in the literature [19]. However, in the literature for SDC – Na_2CO_3 nano-composite, the role of the Na_2CO_3 matrix was not discussed in detail.

An important role in the high ionic conductivity of the SDC – Na_2CO_3 nano-composite was attributed to the amorphous Na_2CO_3 [18]. It was further proposed that at rising temperatures, amorphous nature of Na_2CO_3 may reflect increased disorder of the Na_2CO_3 regions on the SDC surfaces. Therefore, Na_2CO_3 can better protect the surface of SDC and interfaces on a nano-scale and helps to facilitate oxygen ion transportation through the interfacial mechanism [19]. Similarly, for polymer-based composite electrolytes, ion mobility was larger in the amorphous regions, compared to the crystalline ones [20]. Therefore, the amorphous structure was more desirable for higher conductivity in the polymer electrolyte [21]. Composite electrolytes, in which nano-crystalline oxide particles were dispersed in an amorphous matrix, were the focus of attention in solid batteries and hybrid solar cells [22]. In such composite electrolytes, referred as “soggy sand”, ion transport

is mainly facilitated by amorphous regions of the soft matrix and not so much in crystalline parts. The ionic conductivity of amorphous regions was shown to be approximately 10^4 times higher than that of the crystalline phase [21,22].

The design and fabrication of a nano-composite electrolyte with a controlled total interface area between the SDC particles and the Na_2CO_3 matrix for a fixed mass ratio of components is thus the objective of this research paper. Tailoring an SSA enables the activation of the role of interfaces in the conductivity of composite electrolyte. The ionic conductivity and relaxation time of composite electrolyte were measured with electrochemical impedance spectroscopy (EIS). Our investigations were focused on the influence of total interface area between the ceramic particle and the alkali salt at a temperature range of 25 °C–600 °C.

2. Experimental procedure

Two types of samarium-doped ceria (SDC; $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$) powders (Fuel Cell Materials, Ohio, USA) with different particle sizes were used in the experiments. The nanometer-sized powder, referred to hereafter as N20, had primary particle sizes ranging from 5 nm to 10 nm. The micrometer-sized powder, referred to as HP, had a particle size distribution over 60 nm–150 nm. HP powders consisted of hard agglomerates made up of primary particles with 5–10 nm sizes. The measured specific surface areas (SSA) of N20 and HP powders were of $203 \text{ m}^2 \text{ g}^{-1}$ and $11 \text{ m}^2 \text{ g}^{-1}$, respectively. Micrometer-sized SDC (HP) and nano-meter-sized SDC (N20) powders were mixed in the weight ratios of 4.35, 1.35, 0.92, 0.5, and 0.1 to form oxide powders with measured specific surface areas (SSA) of $47 \text{ m}^2 \text{ g}^{-1}$, $93 \text{ m}^2 \text{ g}^{-1}$, $110 \text{ m}^2 \text{ g}^{-1}$, $140 \text{ m}^2 \text{ g}^{-1}$ and $185 \text{ m}^2 \text{ g}^{-1}$. Afterwards, all oxide powders were combined with anhydrous Na_2CO_3 powder (Aldrich, Germany) to form a 10 wt% Na_2CO_3 -SDC composite with specific interfacial area determined by the oxide powder SSA. The influence of the Na_2CO_3 amount in the composite will be discussed in an upcoming publication [23]. The weighed powder mixtures were dry-ball-milled for 6 h by using 3-millimeter diameter YSZ milling media in HDPE bottles. The milled powders were collected and re-ground by hand in an agate mortar and pestle before being uni-axially pressed into a pellet. Pellets made from the composite electrolyte were further subjected to isostatic compaction under 40 MPa in one step, to form a green compact with a diameter of 9 mm and a thickness of 1 mm. The pellets were heat-treated at 700 °C in air for 1 h. The heating rate was 5 °C min^{-1} .

The microstructure of the sintered composites was investigated using a scanning electron microscope (FEG-SEM Leo Supra 35, Oberkochen, Germany) equipped with an energy dispersive x-ray spectrometer (EDS, Roentec, Berlin, Germany). The thermal response of the powder mixtures and the sintered pellets in air was analyzed using a simultaneous thermal analysis system (NETZSCH STA-449C Jupiter, Selb, Germany). The measured water uptake of N20 and HP powders were revealed by TGA to be of 6% and 1%, respectively. The X-ray powder diffraction (XRD) patterns were recorded using a powder diffractometer (Bruker, Karlsruhe, Germany) with Cu K α radiation (1.5418 Å) in the 2θ range of 10° – 90° . A flash-dry silver paste (SPI Supplies, West Chester, USA) was used on both surfaces of the electrolyte pellet to provide electrical contact, covering the full top and bottom surfaces of the pellets. The complex resistivity of the pellets was measured by using a two-probe AC impedance spectrometer with an electrochemical interface (Solartron 1260 and 1286, respectively, Farnborough, UK), and an applied bias voltage amplitude of 100 mV AC. Electrochemical Impedance spectra (EIS) were recorded in the frequency range of 0.1 Hz–10 MHz from room temperature (RT) to 600 °C with a ProboStat™ cell (NorECs, Oslo, Norway) under air atmosphere. A

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