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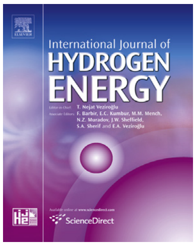

Solid oxide carbonate composite fuel cells: Size effect on percolation

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ABSTRACT

In the studies of solid oxide carbonate composite fuel cell, percolation behaviour of the two phases was investigated as a function of particle size of the oxide phase. The ratio of amount of samarium doped ceria (SDC; $Sm_{0.2}Ce_{0.8}O$) to Na_2CO_3 was varied to determine an optimum ionic conductivity as function of oxide particle size. The roles of both phases in the composite electrolyte were investigated. SDC particles were mixed in different amounts of Na_2CO_3 to obtain composites with carbonate ratios from 1 wt% to 50 wt%. Micro-structural investigations showed that Na_2CO_3 phase served as the matrix in the micro-structure gluing the oxide particles together. The lowest and the highest carbonate ratios caused low conductivities in the composite as in these samples the 3D connectivity of both phases were disrupted. Low conductivity at both ends of the mixture composition could be interpreted as none of the components of the composite dominated the ionic conductivity. The highest conductivity was obtained at 10 wt% Na_2CO_3 amount in the composite electrolyte when nano-sized SDC (5–10 nm) oxide powders were used. Two different particle sizes of SDC powders were used to show that the optimum phase ratio, i.e. percolation of both phases, is function of particle size as well. The conductivity in the composite showed percolation behaviour with respect to the two constituent phases.

Introduction

Solid oxide fuel cells (SOFC) are regarded as a viable alternative energy conversion system for electrical power generation because of their high power efficiencies and tolerance to many different fuels [1,2]. In recent years, in order to achieve more competitive production and operating costs, investigations on solid oxide fuel cells (SOFCs) focussed onto the intermediate–temperature range (between 600 °C and 800 °C) electrolytes. Intermediate–temperature SOFCs, in general, or nano-composite fuel cell, in particular, have a potential for commercial scale production [3].

The performance of the electrolyte can be enhanced by reducing the electrolyte thickness and/or using alternative materials with high ionic conductivities [4]. Among these alternative materials, ceria based alkali carbonate composite electrolyte has an advantage of having a low activation energy for intermediate temperature range when compared to single phase oxide electrolytes like rare-earth doped ceria [5].

The composite electrolytes, in general, are composed of high ionic conductivity oxides, like SDC, coated with alkali salts (carbonate, chloride, hydrate, or sulphate) [6]. The literature on nano-composite electrolyte suggested that the oxide particles provided a skeleton for the composite at operating temperatures [7]. Furthermore, it was shown the electrolyte

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remains as a composite with two stable phases at operating temperatures [7]. Thus, composite electrolytes utilize the best properties of each component. Therefore, SDC based nanocomposites appear to be a promising candidate for the low cost and high conductivity electrolytes [6].

In an SDC based nano-composites electrolyte, SDC phase acts as the oxygen ion conductor, whereas the carbonate matrix was reported as a multiple ion conductor [8–15]. Liu et al., reported that at a 20% weight ratio of Na_2CO_3 the conductivity value peaked at its highest total value of 0.01 S/cm at 481 °C [16]. On the other hand, Rahman et al., observed that the best thermal expansion compatibility with the electrodes was at 50% weight of Na_2CO_3 [17]. Work by Xia et al., showed that composite with 50 wt% carbonate reached 0.1 S cm^{-1} at 600 °C [18]. The average crystallite size of the SDC that was used in that study was 26 nm which was determined from XRD measurements using Scherrer's formula. The difference in the optimum Na_2CO_3 weight ratio appeared to be due to different particle/crystallite sizes of the oxide phase in these two studies [16,18].

The oxide/carbonate based nano-composite materials are very similar in their microstructure to a new class of liquid ionic conductors that attracted the attention as a promising candidate for ion batteries. The liquid ionic conductors consist of dispersed insulating solid oxide particles (*e.g.*, SiO_2, Al_2O_3… etc.) in the liquid non-aqueous lithium salt solutions (*e.g.*, $LiClO_4$ in MeOH, THF… etc.) [19]. In these liquid electrolytes, the dependence of ionic conductivity on the oxide fraction showed a typical interfacial-percolation behaviour. The conductivities of the composite were low for very high or very low concentrations (φ) of the oxide particles (such as insulating silica nano-particles). The peak performance was achieved for intermediate concentrations where both phases of the composite were interconnected in 3D. In addition, for the concentrations with high conductivity, the composites revealed favourable mechanical properties of a soft materials similar to that of 'soggy sand' [20]. This viscous feature and the high conductivities make 'Soggy Sand' electrolytes useful in electrochemical devices such as rechargeable lithium batteries and Dye-Sensitized Solar Cells (DSSCs) [21,22].

In this research paper, ionic conductivity of nanocomposite electrolyte prepared with two SDC powders with different particle sizes were investigated as a function of varied ratios of SDC filler particles to Na_2CO_3 matrix. An optimum ratio of carbonate to SDC was determined for the best ionic conductivity of the composite electrolyte. The investigations were also focused on the Na_2CO_3 percolation phenomena in the SDC-Na_2CO_3 composite.

Experimental procedures

Composite electrolytes with carbonate to oxide weight (wt %) ratios of 1, 5, 10, 15, 20, and 50 were prepared with SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) powders (Fuel Cell Materials, Ohio, USA). Two SDC powders with different particle sizes were used. SDC powders labelled as HP had particle sizes from 0.1 to 0.4 μm with a measured specific surface area of 11 m^2 g^{-1}. SDC powders labelled as N20 had primary crystallite sizes from 5 to 10 nm with a measured specific surface area of 203 m^2 g^{-1}. Na_2CO_3 anhydrous powders were purchased from Aldrich (Germany). The pellets were prepared by mixing weighted powders and dry ball-milling them in dry conditions for 6 h using 3 millimeter-sized YSZ (yttrium-stabilized zirconium) milling balls in HDPE bottles. The milled powders were collected and re-grounded manually in an agate mortar, before they were uniaxially pressed into 9 mm diameter and 1 mm thick pellets. They were then isostatically compressed under 40 MPa. The neat Na_2CO_3 and neat SDC pellets were also prepared through exactly the same procedure as the composites from pure commercial Na_2CO_3 and SDC powders. Then, Na_2CO_3 and SDC-Na_2CO_3 composite pellets were heat treated at 700 °C for 1 h under air atmosphere. The heating rate up to 700 °C was 5 °C min^{-1}. The pure SDC pellets were sintered at 1200 °C for 2 h in air.

Possible chemical reactions and phase distribution of the composites were monitored using X-ray diffraction (XRD) technique. The XRD patterns were recorded on a powder diffractometer with Cu Kα radiation (1.5418 A°) in the 2θ range of 10° and 90°. Microstructures of the sintered composites were 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). A flash-dry silver paste (SPI Supplies, West Chester, USA) was painted on both surfaces of electrolyte pellets as contact electrodes covering the full top and bottom surfaces. The complex resistivity of the pellets were measured by a two-probe AC impedance spectrometer with an electrochemical interface (Solartron 1260 and 1286, respectively, Farnborough, UK), under an applied bias voltage with an amplitude of 100 mV AC. Electrochemical Impedance spectra (EIS) were recorded in the frequency range of 0.01 Hz–10 MHz from room temperature (RT) to 600 °C with a ProboStat™ cell (NorECs, Oslo, Norway) under air atmosphere. A parallel RC equivalent circuit was fitted to high frequency and low frequency data with the Z-View program. The total area of the silver electrodes was used in the conductivity calculations.

Results

The crystal structure of SDC composites with varied concentrations of Na_2CO_3, 1 wt% (~5 vol%), 5 wt% (~12 vol%), 10 wt% (~23 vol%), 15 wt% (~32 vol%), 20wt% (~40 vol%) and 50 wt% (~73 vol%), were determined using the XRD patterns in Fig. 1. The XRD patterns of heat-treated (at 700 °C) composites with different amounts of Na_2CO_3 illustrated similar features. The XRD patterns in Fig. 1 were indexed employing JCPDS card no. 34-394 of crystalline CeO_2 with fluorite cubic structure. After annealing at 700 °C, no impurity or reaction phase, originating from SDC or Na_2CO_3, was detected in the XRD patterns of composites with up to 50 wt% Na_2CO_3 concentrations. However, for composites with 50 wt% Na_2CO_3, weak diffraction peaks were observed in the range of 2θ values from 31° to 40°. The XRD patterns of as-received Na_2CO_3 and commercial Na_2CO_3 carbonate powders after heat-treatment at 700 °C were also shown in Fig. 1. On the XRD pattern of composite with 50 wt% Na_2CO_3, several weak peaks at 2θ values of 30.4°, 37.9°, and 40° were identified as crystalline peaks coming from