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Synthesis and characterization of composite electrolytes based on samaria-doped ceria and Na/Li carbonates

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ABSTRACT

Samaria-doped ceria-based composites with a 2:1 addition of Li and Na carbonates (or simple Na carbonate as admixture) were prepared mixing nanosized powders of the ceramic phase with the remaining constituents. Samples fired at relatively low temperatures (below 700 °C) were characterized by X-ray diffraction, scanning electron microscopy combined with energy dispersive spectroscopy and impedance spectroscopy in air. These composites showed a complex but homogeneous distribution of both phases, with one ceramic skeleton of bonded nanosized grains surrounded by the carbonate-based phase. Impedance spectroscopy data was used to confirm the impressive electrical conductivity of these materials, but also to put into evidence the complex nature of the charge transport process, clearly deviating from classical electrolytes.

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1. Introduction

Fuel cells are unique efficient and environmentally friendly devices for the production of electricity, with hydrogen being the ideal fuel to avoid harmful gas emissions. Systems range from high to low temperature, using a variety of fuels, concepts and cell constituents. High temperature solid oxide fuel cells (HTSOFC) tend to be tolerant to gas impurities, but also require expensive stack materials. Trends in recent years include attempts to lower the operating temperature of HTSOFC. The so-called intermediate temperature fuel cells (ITFC) are expected to be able to meet most goals [1].

Several novel oxygen ionic conductors were developed in recent years, always aiming at lowering the fuel cell operating temperatures [2], but solid electrolytes with the required cost and performance at intermediate temperature are far from

being well established and further developments in this direction are definitely needed.

The state of the art ceramic electrolyte materials are mostly single phase with the bulk ionic transport based on defect hopping between lattice sites. Coexistence of both protonic and oxygen ionic conduction is well established but in general one of the contributions clearly dominates under specific working conditions [3].

The novel so-called ceria-based composite electrolytes include one classical ceria-based electrolyte as dominant phase (usually gadolinia doped ceria or samaria-doped ceria) and one mixture of alkali metal carbonates (usually lithium-LC, sodium-NC or potassium-KC carbonates) as second phase [4–11]. Clues on the coexistence of several charge carriers (carbonate ions, oxygen ions and protons) are obvious but, yet, the exact role of each species as a function of relevant

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parameters seems poorly studied [9,10]. Evidence is also available on a significant role of the oxide phase and/or ceramic/carbonate interface in the composite performance [11,12]. Alternative applications for these materials include devices for the capture of carbon dioxide [13] or carbon–air fuel cells [14].

The range of potential applications, the impressive levels of ionic conduction and the lack of information still available on these systems makes them an interesting subject of study. This work aimed at an improved characterization of the composites microstructure combined with an impedance spectroscopy study as an attempt to highlight the individual features of these materials with respect to conventional electrolytes.

2. Experimental

Composites based on doped-ceria nanopowders and alkali carbonates were prepared using a multi-step process. Samaria-doped ceria (SCO, 20 mol% Sm) was firstly prepared from solutions of nitrates of these cations following a chemical route involving co-precipitation of Sm and Ce-carbonates/hydroxides due to addition of sodium carbonate and ammonia. The resulting precipitate was washed and dried at 120 °C, and afterwards heat treated at 700 °C for 2 h.

The SCO-carbonate composites were prepared combining the previously prepared SCO powder with 30 wt% Na₂CO₃ or (Li, Na)₂CO₃ (Li/Na ratio of 2/1, Table 1). This mixture of carbonates corresponds to a slightly rich Li-containing mixture with respect to the eutectic composition in this binary system [13].

The powder mixture was heat treated at 680 °C for 1 h, and subsequently ground. The composite powders were then pressed into pellets and sintered to nearly full densification at 600 °C for 0.5 h.

All composites were characterized by X-ray diffraction (XRD), scanning electron microscopy combined with energy dispersive spectroscopy (SEM/EDS) and impedance spectroscopy (IS) on Au-electroded samples. Microstructural observations of several samples were preceded by polishing and chemical etching to reveal the special organization of the ceramic phase within the composite. The chemical attack, noticeable by release of gas bubbles, was carried out exposing the surface of the samples to an HCl solution during a few seconds, stopped by immersion in distilled water.

3. Experimental results

Given the composite nature of these materials, the microstructural analysis of these samples was firstly addressed in

detail. Fig. 1(a) and (b) depict typical SEM micrographs of polished samples with (Z1) and without (Z3) Li. The combined SEM/EDS analyses of the Li-containing material revealed a complex microstructure consisting of an intimate mixture of both phases (Fig. 1(a)). At appropriate magnification levels, apparently percolated islands of both phases with dimensions in the order of a few μm can be easily noticed, with the light grey areas corresponding to the ceria-based phase and the darker grey areas corresponding to the carbonates. A similar microstructure could be guessed by EDS for the Na₂CO₃/SCO composites, although clear images were impossible to obtain due to extreme reactivity of the polished surface with the surrounding atmosphere (most likely with water vapor) which leads to the formation of fiber-like precipitates (Fig. 1(b)).

The exposure of the surfaces to hydrochloric acid revealed a clearer picture (Fig. 1 (c) and (d)), with the formation of clean pores and NaCl crystals as the result of the reaction between the acid and the alkali carbonates. It should be noticed that Li cannot be detected by EDS.

Details of the microstructure of the oxide phase are shown in Fig. 1 (e) and (f). The delicate SCO ceramic skeleton is clearly visible in both cases, consisting of nanosized grains bonded to each other even after chemical etching, showing an early stage of sintering of this phase irrespective of the relatively low firing temperatures used in the process. Moreover, while differences in densification can be hardly quantified, the composition of the carbonate has a significant impact on grain growth, with grain sizes in the order of 100 nm for the Li-containing sample (Z1) and smaller (<50 nm) for the sample without Li₂CO₃ (Z3). This sintering aid effect is likely to be related to the formation of liquid phase associated to the LC–NC eutectic at about 500 °C [13] and should provide additional mechanical resistance to these samples. Due to the presence of large voids between the ceramic grains, percolation of the carbonate-based phase is also obvious.

Powder XRD data showed negligible phase interaction. All patterns were dominated by the fluorite-type SCO, whereas smaller additional peaks could be ascribed to the carbonate phases, presumably predominantly amorphous.

Overall, these observations showed the successful production of a ceramic skeleton based on SCO, with nanosized grains, surrounded by a mixture of amorphous carbonates. Both phases provide a continuous pathway for ionic transport and a large interfacial surface area, considering the grain size of the ceramic phase. To our knowledge this is the first time that the microstructural features of these materials are observed and reported in such detail.

Impedance spectroscopy measurements carried out in air between 200 and 550 °C confirmed the high electrical conductivity of these composite materials and the relevance of the carbonate phase on the overall performance. Although the envisaged working temperatures for these materials should exceed about 500 °C, to benefit from the conductivity onset at this temperature described later in this text, a series of comments on the lower temperature performance are expected to help in highlighting the specific characteristics of these materials.

One set of impedance results obtained at 350 °C is shown in Fig. 2. These spectra include (at least) what seems to be one depressed arc related to the bulk composite response and one

Table 1 – Composition, designation and electrical conductivity of samples.

Sample designation	Composition		Conductivity (S/cm)	
	LC + NC wt%	Li/Na molar ratio	at 400 °C	at 500 °C
Z1	30	1:2	1.9×10^{-4}	2.0×10^{-1}
Z3	30	0	1.3×10^{-4}	7.9×10^{-4}

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