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Impact of ceramic matrix functionality on composite electrolytes performance

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ABSTRACT

Ceria-based composite electrolytes (50 and 70 vol%) including one mixture of Li and Na carbonates (1:1 molar ratio) were prepared using either pure CeO_2 (modest conductor) or Gd-doped ceria (excellent oxide-ion conductor) as ceramic matrix. The composite electrolytes and their phase constituents were tested under pure CO_2, air, and H_2 diluted in N_2, at temperatures ranging from 300 to 580 °C, to study their electrical performance. Impedance spectroscopy measurements performed under these working conditions were complemented by microstructural characterization. Low temperature (below melting) impedance shows in a clear manner the relevance of the matrix functionality on the performance of these composites, but also reveals additional microstructural and even unusual composite effects. These data were used to test equivalent circuit models derived from the composite constituent properties, and to assess their potential to design composites for target functionalities at higher temperature.

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1. Introduction

Fuel cells are considered a key technology for the production of electrical power in a sustainable energy scenario where hydrogen is used as fuel. However, fossil fuels still play a significant role in energy supply. Natural gas, widely used, is mostly suitable for operating temperatures in excess of 500 °C where only solid oxide fuel cells (SOFC) or molten carbonate fuel cells (MCFC) might operate. These systems are more tolerant to gas impurities and run without external gas reforming or expensive catalysts [1,2].

Composite electrolytes including one oxide-ion conductor (usually ceria-based) and one mixture of alkaline carbonates emerged as potential candidates for fuel cells for intermediate temperatures (around 500–600 °C) [3–18]. However, the range of applications of these materials extends also to carbon dioxide separation membranes [19–22]. These materials possess oxide and carbonate-ion conductivity due to the role of the constituent phases, but also significant protonic conductivity, apparently along the oxide/carbonate interface or via “hopping” between neighboring hydrogen carbonate and carbonate ions. Given the high ionic conductivity of molten carbonates with respect to ceria-based oxide-ion conductors, usually the dominant charge carriers are the carbonate ions with the oxide-ions and protons as second and third contributors [11,17].

In previous work we have tried to inspect specific characteristics of these materials. The analysis of the roles of grain size, chemical nature of the ceramic matrix and interaction of these composites with the atmosphere pointed toward a complex range of influential parameters. One critical aspect is the drift in the composition of the electrolyte. Nominal compositions might deviate due to partial loss of carbon dioxide from the carbonates, with formation of alkaline oxides. Combination with environmental moisture or hydrogen might yield extrinsic species like hydroxide or hydrogen carbonate ions [13,14,18].

Work in the field of molten carbonates supports recent findings in the study of composite electrolytes. Changes in the gas phase composition (namely in O_2 and CO_2) affect the acid-base behavior of the molten salt and impact the concentration of several species (e.g., oxide, peroxide and superoxide ions, or even dicarbonate ions) [23–28]. Hydrogen carbonate ions are reportedly formed in the presence of water or hydrogen [29].

Exact matching of oxide and carbonate-ion transport is essential for CO_2 separation membranes, one of the most interesting applications for these composite electrolytes. The net flow of CO_2 through the membrane is the result of counter transport of oxide and carbonate ions. However, there is little basis for the compositional and microstructural design of these composites. Information available corresponds to specific compositions, microstructures and working conditions, and all these parameters are influential [19–22].

Attempts to discriminate the role of each ion were mostly based on classical dc techniques involving seals to separate distinct cell environments [11,17]. Since gas phase composition affects the ionic transport in these materials [18], this means that such experiments provide information on mixed working conditions where extreme cell regions behave differently. The information thus obtained is on average transport properties. In the present work an attempt is

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made for the first time to inspect the potential of impedance spectroscopy to discriminate the role of oxide-ions, based on equivalent circuits taking into consideration the composite nature of these materials and multi-ionic transport.

To reach this goal, we have exploited the functionality of the ceramic matrix (in this case the oxide-ion conductivity) on the performance of these composite electrolytes. A series of experiments was planned using both one excellent oxide-ion conductor (Gd-doped ceria, hereby named CGO) and one modest conductor (pure ceria). The electrical properties of "pure" materials depend on nature and amount of minor impurities. However, it is commonly accepted that CeO_2 is a poor electronic conductor in air and a modest mixed ionic and electronic conductor under reducing conditions, due to formation of oxide-ion vacancies in parallel with the reduction of Ce^{4+} to Ce^{3+} in the lattice [30,31].

The selection of ceria-based ceramics for this study has two major reasons. Firstly, doped ceria electrolytes (e.g., with Gd^{3+} or Sm^{3+}) are suitable oxide-ion conductors already tested in these composites, chemically stable in contact with the corrosive molten carbonates environment. Secondly, pure CeO_2 is the closest ceramic matrix able to ensure distinct matrix performance with minimum changes in the chemistry of these systems. $LiAlO_2$ would be a reasonable alternative for being the usual matrix in MCFC, but the chemical nature of this phase is by far distinct from ceria.

2. Experimental

Ceria-based composite materials (50 and 70 vol% of the ceramic phase) were prepared from $Ce_{1.9}Gd_{0.1}O_{1.95}$ (CGO, from Praxair, average powder particle size exceeding slightly 100 nm) and CeO_2 (from Sigma–Aldrich, average powder particle size smaller than 25 nm) and one mixture (1:1, molar ratio) of Li and Na carbonates (Sigma–Aldrich). Volume percentages of constituent phases here mentioned correspond to those derived from simple dosage of constituents, and disregard the presence of porosity in the fired composites. The adopted procedure was previously described, and involved high energy milling with zirconia-based balls (3 mol% Y_2O_3, from Tosoh Co.) in Nylon containers. Besides intimate mixture, room temperature chemical interaction between constituents is also achieved, namely with formation of $NaLiCO_3$ (NLC) [13,14].

Powders of all composites were uniaxially pressed (220 MPa) as disks with about 10 mm diameter and 2 mm thick. One single thermal treatment at 690 °C, for one hour, with constant heating and cooling rates of 5 °C/min, produced composite samples of appropriate mechanical strength for further testing. Disks of CGO and CeO_2 were sintered at 1550 °C, for 4 h, to be used as reference. With a similar goal, one disk of NLC was also prepared firing one pressed pellet close to the eutectic temperature of this system, around 500 °C.

Impedance spectroscopy measurements were performed under pure carbon dioxide, air and one mixture of nitrogen and hydrogen (10 vol% H_2) in the temperature range 300–580 °C. One distinct sample was used for each gas to avoid potential "memory" effects derived from interaction with a given atmosphere (e.g., formation of new species and/or partial decomposition). The H_2-based gas mixture generates a reducing condition typical of anodic fuel cell compartments. The exact oxygen partial pressure is determined by the H_2/H_2O partial pressure ratios, with water being formed from minor oxygen sources. In the case of "pure" CO_2, where the relevant chemical equilibrium involves the CO_2/CO couple, the dominant CO_2 concentration generates a rather mild oxidizing condition when compared to the previous gas mixture.

Samples for electrical measurements were painted with porous Au-electrodes, fired at temperatures below but close to the sintering temperature. All high-temperature electrical connections were also made with Au-leads. One HP 4284 A LRC Meter was used to study the cell impedance with 0.5 V ac test signal amplitude, in the 20 Hz to 1 MHz frequency range. The impedance spectra were fitted to equivalent circuits using the software ZView v3.0. Besides the fitting error parameters implemented in the program, we have also plotted the relative deviations of the real ($\Delta Z'$) and imaginary ($\Delta Z''$) parts of the impedance (Z_{exp}) as a function of the frequency – the fit quality plot, according to Boukamp [32]. Here, $\Delta Z' = (Z'_{exp} - Z'_{cal})|Z_{exp}|^{-1}$ and $\Delta Z'' = (Z''_{exp} - Z''_{cal})|Z_{exp}|^{-1}$, with the subscripts denoting the experimental and the calculated values of Z' and Z''.

As a complement to these characterization techniques, scanning electron microscopy (SEM, Hitachi SU-70), equipped with one energy dispersive x-ray detector (EDS, Bruker QUANTAX 400) was also used to try to identify microstructural and compositional changes, namely in samples showing the most diverse electrical performance. To highlight grain growth of ceramic particles after sintering at low temperature, the (nanosized) CeO_2 powder particles were also observed by transmission electron microscopy (TEM, Hitachi H9000). The top/bottom and fracture surfaces of sintered samples were especially inspected to identify possible surface effects. XRD (Rigaku Geigerflex D/Max-C series diffractometer, using Cu Kα radiation) confirmed previous results where no chemical interaction was found between the ceramic phase and the mixed carbonates [14], for which reason the corresponding information is reduced here to this short reference.

3. Results and discussion

3.1. Microstructural characterization

The microstructural characteristics of composites with 50 or 70 vol% of ceramic phase are shown in Fig. 1(a)–(d). They closely match previously reported features of similar materials [13,14,18]. In the case of only 50 vol% of CGO (Fig. 1(a)), the ceramic phase (light gray grains) is mostly surrounded by a darker phase consisting of mixed carbonates. Part of the grains is interconnected but many grains seem isolated within the carbonate phase. This means that the ceramic phase contiguity is modest for this composition, although ensuring enough strength to preserve the mechanical integrity of the samples above the carbonates eutectic temperature (around 500 °C). This issue will be further addressed in the following paragraphs.

The general features observed for the 50 vol% CGO based composites (Fig. 1(a)) can be repeated in the case of CeO_2-based composites (Fig. 1(b)). The only meaningful difference is that CGO grains are slightly larger than those of CeO_2, showing the impact of the distinct particle size of precursor powders.

Sintered CeO_2-based composites (50 vol%) were also washed with diluted HCl to remove the carbonate phase, to put into evidence the ceramic backbone (Fig. 1(e)). The corresponding starting powder grain size can be observed in Fig. 1(f). Incipient sintering and formation of a feeble ceramic backbone is clearly noticed even with the low sintering temperatures employed. This idea of a stable ceramic skeleton could also be confirmed during and after impedance spectroscopy measurements performed up to about 580 °C using a spring loaded cell, where the cell preserved the overall dimensions and shape.

On increasing the ceramic content to 70 vol%, the contiguity of the ceramic phase increases, as expected (Fig. 1(c) and (d)). The impact of increasing oxide content is a reinforcement of the ceramic backbone. We emphasize here that the ceramic phase is contiguous (as well as the carbonates), with enhanced grain to grain bonding

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