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# Relevance of the ceramic content on dual oxide and carbonate-ion transport in composite membranes

Cátia M.C. Soares, Sónia G. Patrício, Filipe M.L. Figueiredo, Fernando M.B. Marques\*

Department of Materials & Ceramic Engineering/CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

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## ABSTRACT

Composite electrolytes based on Gd-doped ceria (from 50 to 95 vol%) and one eutectic mixture of sodium and lithium carbonates were prepared by co-firing, in order to identify the compositional range where both oxide and carbonate-ion transport are balanced, as required for high performance CO<sub>2</sub> separation membranes. Considering the adequacy of this technique, the effects of composition and microstructure on oxide-ion transport were inspected by impedance spectroscopy. The specific features of low temperature impedance spectra allowed access to data on oxide-ion transport based on a hereby suggested equivalent circuit where the individual characteristics of both constituent phases are considered, as well as the variable nature and relevance of interfaces. Combined analysis of all information indicates that the range of interesting compositions for balanced dual ionic conduction corresponds to a ceramic phase content around 85 vol%, for the present microstructural characteristics and a target temperature below 550 °C.

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## 1. Introduction

Molten carbonates are mostly known as electrolyte materials for molten carbonate fuel cells (MCFC) but they can also be used as carbon dioxide concentrators because of their capability to transport CO<sub>2</sub> as CO<sub>3</sub><sup>2-</sup> ions [1,2]. This highlights their possible application in carbon capture and storage (CCS), namely in fossil-fuelled power plants [3,4]. This technology can be applied to separate CO<sub>2</sub> from flue gas, as well as from H<sub>2</sub>, when syngas is converted into the latter eco-friendly fuel using the water-gas shift reaction. Given the still wide dependence on fossil fuels, CCS is regarded as the near-term solution to ensure control of CO<sub>2</sub> emissions.

Since molten carbonates are unable to be self-shaped as functional membranes, their immobilization into a ceramic

matrix is the adopted solution to produce devices like fuel cells. While in the field of MCFC the standard ceramic matrix is based on LiAlO<sub>2</sub> [5,6], ceria-based ceramics have been suggested as an alternative for other applications [7–20]. Ceria-based composites are widely studied as electrolytes for intermediate temperature fuel cells due to their excellent ionic conductivity [9,13–20]. They possess oxide and carbonate-ion conductivities inherent to the composite phase constituents, but also significant proton conductivity under specific conditions [16,21–23]. Multi-ionic conduction opens new horizons for advanced applications. For instance, proton conductivity observed in these composite electrolytes can be employed for the electrochemical synthesis of ammonia [10], while dual oxide and carbonate-ion transport can be used for CO<sub>2</sub> separation membranes [11,24–27].

\* Corresponding author. Tel.: +351 234370269; fax: +351 234370204.

E-mail address: [fmarques@ua.pt](mailto:fmarques@ua.pt) (F.M.B. Marques).

Currently, the application of ceria-based carbonate composites in CCS attracted great interest due to the exclusive selectivity inherent to the counter-flow of oxide and carbonate-ions. Microporous inorganic membranes show no equivalent CO<sub>2</sub> selectivity. Moreover, dual ionic transport requires neither electrodes nor external power sources, being quite attractive when compared with the MCFC based CO<sub>2</sub> concentrators. Despite their promising properties, the CO<sub>2</sub> permeation flux is still modest [11].

Up to now, the quest of efficient materials design strategies leading to high CO<sub>2</sub> permeation flux is almost disregarded in the literature. Modelling studies showed that the improvement of CO<sub>2</sub> permeation rate relies on tuning the oxide-ion conductivity of the solid oxide phase [28,29]. One approach is to focus on the nature of the ceramic oxide-ion conductor. However, most ceramic oxide-ion conductors show high reactivity against molten carbonates. This is the case of yttria-stabilized zirconia which tends to form lithium zirconate in the presence of lithium carbonate [11]. Other ceramic oxide-ion conductors like bismuth-based oxides show reversible phase transformations at high temperature, taking long time to reach a steady state [26].

Regardless of the chemical composition of the constituent phases, the microstructure of composite membranes should maximize the flux of oxide and carbonate-ions, which basically corresponds to equalize the conductance of two phases. In principle, this should be easily achieved taking into account the potentially large difference between the conductivity of both phases (roughly 1 Scm<sup>-1</sup> for the molten carbonates versus 0.01 Scm<sup>-1</sup> for ceria-based electrolytes, at 650 °C [30,31]). Assuming a simple mixing rule and those reference conductivity values, it is possible to obtain a composite conductivity of 0.1 Scm<sup>-1</sup> with just 10 vol% of carbonate in a ceria-based matrix. This crude model assumes that the conductivity of each phase is not disturbed in the composite, which obviously is difficult to achieve for some microstructures, namely if a film of carbonates covers entirely the ceramic particles.

Herein, we explore the role of the oxide volume fraction to identify the compositional range where the transport of both oxide and carbonate ions is properly balanced inside the composite. To achieve this purpose, gadolinium-doped ceria (CGO) was used as oxide-ion conductor matrix due to its well-known high conductivity and chemical stability against molten carbonates. The simplest processing route (powder mixture and sintering) was selected to produce the composites, and their total electrical conductivity was carefully inspected by impedance spectroscopy to try to identify specific features providing a clear insight on the contribution of each phase. An attempt is presented to correlate the low temperature impedance spectra with an equivalent circuit adjusted to the electrical microstructure, aiming at an assessment of the partial conductivities of the composites. The final goal is to obtain additional tools for the design and testing of high-performance dual-phase composite membranes with fine-tuned ceramic backbone microstructures.

## 2. Experimental

Composite materials based on Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (Praxair, S<sub>BET</sub> = 11.5 m<sup>2</sup> g<sup>-1</sup>) and one eutectic mixture of sodium and

lithium carbonates (Sigma–Aldrich, 48:52 molar ratio) were mixed with different volume ratios, as listed in Table 1. Here, nominal volume percentages of constituent phases do not take into account the role of porosity within the co-fired composites. Composite powders were prepared by high energy milling to promote the formation of NaLiCO<sub>3</sub> (NLC) [18]. Typically, high energy milling was carried out in a planetary ball mill with Nylon containers and zirconia-based balls (balls to powder mass ratio of 10:1, respectively). Afterwards, powders were uniaxially pressed (40 MPa) as disks with about 8 mm diameter and 2 mm thick and then submitted to isostatic pressure (200 MPa). The green pellets were sintered at 690 °C for 1 h.

The composite processing conditions were adopted after exploitation of several alternative processing steps, including pre-melting of alkaline carbonates before mixing with the ceramic, low and high energy milling of individual precursors and composite powder mixtures, reduction of the ceramic grain size by milling or coarsening by thermal treatment, single uniaxial and combined uniaxial and isostatic pressing, amongst other parameters. Most of these results were reported elsewhere [17–18,32–33]. While there is no unique set of effective processing conditions, temperature tends to be critical since lower firing temperatures prevent the consolidation of the ceramic skeleton (no mechanical robustness above melting) and higher firing temperatures enhance sintering, decreasing the interfacial area between phases [34]. Furthermore, alkaline carbonates decompose at high temperature.

Two additional samples consisting of the individual constituent phases were also prepared to be used as reference. CGO was sintered at 1550 °C for 4 h, while NLC was fired at 490 °C during 1 h (below the eutectic temperature, which is ~500 °C).

Microstructural characterization was performed by scanning electron microscopy (SEM, Hitachi SU-70) coupled with one energy dispersive X-ray detector (EDS, Bruker Quantax 400). Specific surface areas of sintered composites were determined by BET (S<sub>BET</sub>, Brunauer, Emmett and Teller) based on the N<sub>2</sub> adsorption at -196 °C (Micrometrics Gemini 2380). Prior to analysis, samples were outgassed under vacuum at 200 °C overnight.

The electrical conductivity was evaluated by impedance spectroscopy (IS, HP 4284A LCR Meter) using a test signal amplitude of 0.5 V ac (lower values were also applied to distinguish electrode contributions) within the 20 Hz to 1 MHz frequency range (frequencies logarithmically spaced with 10 points per decade). Prior to the electrical measurements, composite samples were painted with gold paste as electrodes

**Table 1 – Acronyms, compositions, specific surface areas, and activation energies (E<sub>a</sub>) at low (LT) and high temperatures (HT) of CGO-based composites.**

Composite sample	Volume ratio CGO:NLC	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	E <sub>a,LT</sub> (kJ mol <sup>-1</sup> )	E <sub>a,HT</sub> (kJ mol <sup>-1</sup> )
CGO50	50:50	1.64	102	28
CGO70	70:30	2.87	105	37
CGO85	85:15	3.25	96	41
CGO95	90:5	4.12	92	46

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