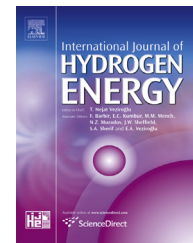


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Ionic transport in (nano)composites for fuel cells



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ABSTRACT

Several composite materials were produced using ceria nanoparticles (<25 nm) and LiAlO₂ (particle size >1 μm). The oxides were combined with a mixture of Na₂CO₃ and Li₂CO₃ (eutectic composition), and fired at temperatures in the 600–700 °C range (vacuum assisted in a few cases). The composites were characterized by scanning electron microscopy, X-ray diffraction and impedance spectroscopy, in air, in the 300–600 °C range. Irrespective of composition or grain size all samples exhibited the same type of conductivity dependence on temperature, with a steep change close to the carbonates eutectic temperature. At T > 500 °C all materials have identical conductivity, indicating that molten carbonates dominate the electrical performance. However, at low temperature (300–450 °C) significant differences can be noticed in all composites, with the best performance observed for ceria based composites with larger grain size (close to 135 nm).

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Introduction

Ceria-based composites including mixtures of alkaline carbonates are currently studied as electrolytes for fuel cells, CO₂ separation membranes, steam electrolysis and electrochemical synthesis of ammonia [1–11]. Such applications rely on the presence of multiple ionic charge carriers in these systems. The usual ceramic phases (e.g., Gd-doped ceria, CGO) are well-known oxide-ion conductors, unless under reducing conditions where the electronic conductivity becomes relevant [12,13]. However, in composites with molten alkaline carbonates we can find reference to a wide range of ions, with alkaline, carbonate, oxide and protons often mentioned [14–18]. In fact, besides intrinsic ions, molten carbonates easily interact with gas phase species like water vapor, carbon dioxide or even hydrogen. In such cases ions like dicarbonate, hydroxide or hydrogen carbonate are also formed.

Furthermore, intrinsic ions are believed to be locally associated [19–24].

The role of the ceramic backbone grain size on the composite transport properties is also a subject of debate [25,26]. The usually invoked nanocomposite effect corresponds to boosted proton conductivity when the ceramic backbone has nanosized ceramic particles. This effect would be related to high interfacial proton conduction along the ceramic/salt interface [27] or the possibility of a combined mechanism involving protons progressing between neighbor hydrogen carbonate and carbonate ions [28].

Claimed proton conductivity finds support on the possibility to run a fuel cell exclusively with hydrogen as fuel [29], the formation of water vapor in the cathode side [30] or the capability to drive the electrochemical synthesis of ammonia [9]. However, some of these conclusions are based on short term tests (e.g., with fuel cells) and can find alternative explanations like simple hydrogen leaks, diffusion across the

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liquid phase in the composite or even the combined role of alternative ionic species.

The possible conductivity enhancement with nanosized ceramic matrices is also a subject of controversy. We find few studies on the role of the ceramic particle size on the composite performance [25,26]. In composites based on CGO powders with particle size ranging from 45 nm to 16 μm , materials with larger grain size showed higher conductivity. The formation of thin layers of alkaline hydroxides after light decomposition of the carbonates and reaction with environmental moisture was suggested, due to visible vestiges of a new phase in the composites involving larger grain size [25]. With residual open porosity such surface effects could occur across the entire composite thickness, providing a parallel pathway for ionic transport. So, enhanced conductivity might be obtained based on the contribution of foreign charge carriers, masking grain size effects.

Previous work provides negligible information on the microstructural characterization of tested composites (e.g., porosity, grain size distribution), a key parameter in materials performance. Processing of dense composites also deserved little attention. Common processing routes include simple mixing and firing of both constituents. However, sintering temperatures constrained by the relatively easy decomposition of alkaline carbonates at high temperatures. As alternative, in a two-step route, a ceramic backbone is consolidated at high temperature ($>1400\text{ }^\circ\text{C}$) before impregnation with molten carbonates at lower temperature ($<800\text{ }^\circ\text{C}$). Light vacuum can be used to assist the process efficacy [11,31].

Nanocomposites can hardly be produced using the second methodology due to fast grain growth at typical oxide sintering temperatures ($>1400\text{ }^\circ\text{C}$). One alternative is a chemical route where all phases are obtained at modest temperatures from a mixture of adequate precursors [32,33]. Also, when adopting joint firing, consolidation of the composite is quite easy at low temperature ($<700\text{ }^\circ\text{C}$). Liquid phase assisted sintering favors bonding between ceramic particles, situation confirmed in ceria-based systems [34]. However, this process is only able to produce samples with feeble mechanical properties and large porosity.

In this work, an alternative processing method is introduced, blending mentioned routes. Mixing and low temperature firing of composite constituents was combined with the application of light vacuum. Densification was enhanced at quite low sintering temperature ($700\text{ }^\circ\text{C}$) while grain growth was hampered. Changing firing temperatures and the vacuum condition (with and without vacuum) also yielded distinct average grain sizes (by a factor of about 2) as needed in order to test the role of the ceramic grain size on transport properties.

In previous work, a slightly higher conductivity was noticed at low temperature (below the carbonates eutectic) for composites based on pure ceria with respect to those based on CGO [35]. This justified the present adoption of pure nanosized ceria powder as reference oxide phase. However, to assess the role of the ceramic phase on the global transport properties a second set of samples was produced using LiAlO_2 . This mixed oxide is the standard matrix used in Molten Carbonate Fuel Cells (MCFC). Interestingly, there is no previous attempt to compare the performance of ceria-based nanocomposites

against the performance of standard MCFC composite electrolytes, situation here exploited.

Impedance spectroscopy can be successfully used to study the transport properties of these composites [36,37]. This was the main analytical tool used to assess the composites performance. Microstructural and structural characterization complemented the electrical characterization.

Experimental

The main materials used in this work were Li and Na carbonates (from Sigma Aldrich, 99% purity) and ceria (from Sigma Aldrich, average particle size below 25 nm). Li and Na carbonates were mixed in the proportion corresponding to the eutectic composition (close to 1:1 M ratio), melting at about $499\text{ }^\circ\text{C}$. This mixture will be hereby named NLC. The oxide and the mixed carbonates were combined in a 50:50 vol% proportion.

Samples were prepared using distinct firing conditions to assess the role of grain size on performance. The processing route sequence started with joint mixing/milling of ceria and NLC using high energy milling, before uniaxial pressing and firing at 600 or $700\text{ }^\circ\text{C}$ for 1 h. Light vacuum (standard lab water jet vacuum pump) was applied in some cases during the final sintering stage to facilitate the removal of trapped air bubbles from the composite. Typical dimensions of sintered samples were 8 mm in diameter and 2 mm thick. The ceria powder was also used to prepare samples for electrical conductivity measurements and obtain reference data on this phase. Sintering was at $1550\text{ }^\circ\text{C}$, for 4 h, and the resulting ceramics were fully dense.

A second series of composite samples (hereby named as LA) was produced using LiAlO_2 as ceramic phase. In this case the chemical used was a standard LiAlO_2 Sigma Aldrich powder with nominal 99% purity. Due to systematic problems (melting of samples while sintering) when processing pellets of this precursor, the as received powder was studied by XRD

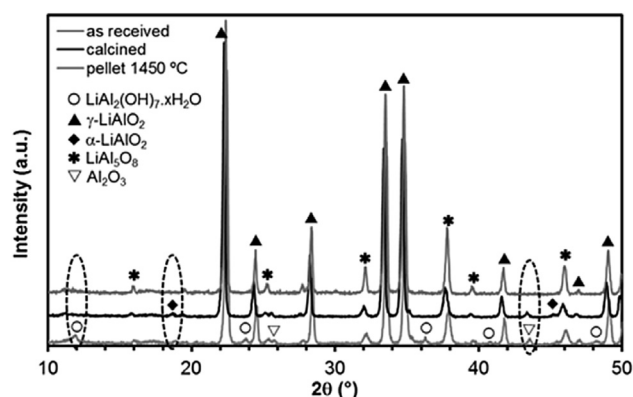


Fig. 1 – XRD patterns of LiAlO_2 . From bottom upwards: as received, after calcination at $800\text{ }^\circ\text{C}$ for 10 h, and from a pellet sintered at $1450\text{ }^\circ\text{C}$. Detectable changes in phase composition with thermal and storage history, even when minor, are believed to be influential in the performance of composites based on LiAlO_2 .

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