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Composite electrolytes for fuel cells: Long-term stability under variable atmosphere

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ABSTRACT

Ceria-based composites (50 vol% of the ceramic phase) including one mixture of Li and Na carbonates (1:1 molar ratio), were prepared using either pure ceria (modest conductor) or Gd-doped ceria (excellent oxide–ion conductor) as ceramic matrix. These materials were aged for periods of up to 1000 h at 550 °C, under pure CO₂, in air and in H₂ diluted in N₂, to test their stability and electrical performance. Impedance spectroscopy measurements performed between 300 and 600 °C were complemented by structural and microstructural characterization. The excellent long-term stability in CO₂ drops slightly when moving to air and in a pronounced manner when moving to diluted H₂. In all cases and in all conditions the best performance is observed for pure ceria-based composites. Electrode (Au) and electrolyte degradation were found interrelated.

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1. Introduction

Intermediate temperature fuel cells (for 600 °C or even lower) may operate with natural gas without external reforming or expensive catalysts. Such operating temperatures are below those commonly used in solid oxide fuel cells (SOFCs) or molten carbonate fuel cells (MCFCs). This explains the continuous interest in the progressive adjustment of these systems (materials and concepts) to these operating conditions [1]. In the case of solid electrolytes, ceramics with high conductivity at such temperatures (e.g., Bi-based electrolytes) also show poor stability, often significant electronic conductivity under reducing conditions, which prevents their utilization [2]. Alternative materials are highly desirable for this reason.

Composite electrolytes emerged as potential candidates for intermediate temperature fuel cells, carbon dioxide separation membranes, steam electrolysis and even synthesis of ammonia [3–21]. These electrolytes include a porous matrix frequently made of classical ceria-based electrolytes used in SOFCs (Gd or Sm-doped), instead of the usual LiAlO₂-based matrix of MCFCs. A mixture of alkaline carbonates is the second phase in these composite electrolytes, in all aspects similar to the classical mixed salts used in the latter system. The most obvious distinction between these composite electrolytes and those used in the classical MCFCs concept is the oxide–ion conductivity of the ceramic matrix.

The wide range of applications of these materials relies on mixed ionic conduction. Besides oxide and carbonate–ion conducting phases (ceramic and molten carbonates, respectively), these composites also show significant protonic

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conductivity, presumably along the oxide/carbonate interface or via “hopping” between neighboring hydrogen carbonate and carbonate ions [10,16]. The potential role of alkaline ions on global charge transport cannot be discarded as well.

High temperature impedance spectra of cells based on these materials (above the carbonates melting) shows only the electrode contribution, enabling merely the assessment of the total electrolyte resistance. On the contrary, recently we have shown that low temperature impedance data provides information on the ceramic matrix functionality, namely if oxide-ion conductor [22]. We follow here this type of approach monitoring long-term ageing, the central subject of this study. In fact, little information is available on the issue of long-term stability of these composite electrolytes. We find mostly positive comments on performance but based either on short tests or limited ranges of working conditions [10,19].

Interestingly, one critical aspect in the performance of these composite electrolytes is their potential drift in composition. Departure from nominal composition due to partial loss of carbon dioxide with formation of alkaline oxides is one of the most obvious reasons. As a consequence, these materials also combine readily with moisture to form hydroxides [12,13]. Changes in the gas-phase composition (namely in O_2 and CO_2) influence the concentration of a wide range of species like oxide, peroxide or even dicarbonate ions within the molten carbonates, with intricate impact on electrical performance [21,23–28]. Hydrogen carbonate ions are other relevant species formed after exposure to water or hydrogen [29]. Lastly, different diffusivities of the various alkaline metals in the mixed carbonate melt may also be a source of compositional changes during fuel cell operation [30]. Altogether, these comments put into evidence the need for a detailed assessment of the stability of these composites under a diverse set of working conditions. This was the motivating idea behind this work.

To reach this goal, a series of experiments was planned using both one known oxide-ion conductor (Gd-doped ceria, hereby named CGO) and one modest conductor (pure ceria). Ceria-based oxide-ion conductors are the most suitable and widely used ceramic phases in these composite electrolytes, assumed as chemically stable in contact with the molten carbonates. Considering the goal of this work and aiming at the assessment of potential selective lixiviation of dopant (Gd) from solid solution, after prolonged contact with the molten carbonates, pure ceria was also tested as ceramic matrix and as reference. Exploited gas-phase compositions included pure carbon dioxide, air and also hydrogen containing gas mixtures. Carbon dioxide is expected to be the best environment for the preservation of the carbonates. Air and hydrogen simulate typical oxidizing or fuel/reducing environments, of special interest when attempting to operate in CO_2 -free fuel cells.

2. Experimental

Ceria-based composite electrolytes (50 vol% of the ceramic phase) were prepared from commercially available $Ce_{1.9}Gd_{0.1}O_{1.95}$ (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). The adopted procedure was previously described, and involved high energy milling with TZP balls (zirconia with 3 mol% Y_2O_3 , from Tosoh Co) in Nylon containers. Room temperature mechano-chemical interaction between constituents is achieved in this manner, with formation of $NaLiCO_3$ (NLC) even before any thermal treatment [12].

Powders 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 under constant heating and cooling rates (5 °C/min) produced samples of suitable mechanical strength for further testing. A set of samples consisting exclusively of the pure phases (CGO, ceria and mixed carbonates) was also prepared based on the precursor powders, after pressing and sintering at adequate temperatures (1550 °C for 4 h in the case of the oxides, 490 °C for 1 h in the case of the mixed carbonates). These samples were used to obtain further insight on the relative performance of the composites with respect to their constituent phases.

After shaping and sintering, the composite electrolytes were Au-electroded before ageing, for periods of 0, 100, 250 and 1000 h, at 550 °C. These tests were conducted inside closed chamber cell holders under carbon dioxide or one mixture of nitrogen and hydrogen (10 vol% H_2), with flow rates around 50 ml/min. Treatments in air were performed within an open air furnace chamber, without forced convection. All ageing tests were performed with freshly prepared samples. Ageing was discontinued after confirmation of either degradation (in 10 vol% H_2) or stability (in CO_2) of the cells performance after 250 h.

Impedance measurements were performed in the temperature range 300–600 °C before and immediately after ageing, without removal from the cell chamber used in ageing experiments, to preserve the cell condition. All electrical connections were made with Au-leads. One HP 4284A 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.

As a complement to this characterization, scanning electron microscopy (SEM, Hitachi SU-70), equipped with one energy dispersive X-ray detector (EDS, Bruker QUANTAX 400) was used to identify possible microstructural and compositional changes. The top/bottom and fracture surfaces of samples were especially inspected to identify possible surface effects. Phase stability was studied using powder X-ray diffraction (XRD, Rigaku Geigerflex D/Max-C Series).

3. Results and discussion

The microstructural characteristics of these composite electrolytes shown in Fig. 1 are in all aspects similar to those previously reported for similar compositions [12,13]. The ceramic phase (light gray grains) includes interconnected grains but also grains loosely bonded or even hanging within the carbonate phase, corresponding to a moderate ceramic percolation, as evidenced by the higher magnification micrographs. These microstructures also demonstrate that the relative grain size of the starting powders is preserved after sintering, with the average grain size of CGO particles slightly higher than found for pure ceria (e.g., Fig. 1(a) versus Fig. 1(c)).

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