MIXED IONIC CONDUCTION IN HOMOGENEOUS AND LAYERED COMPOSITE ELECTROLYTES

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Introduction

Fuel cells are promising systems for the production of electricity from hydrogen or fossil fuels. High temperature fuel cells (HTFC), based on ceramic electrolytes, tolerate fuel impurities but require expensive stack materials to survive to demanding operating temperatures. Low temperature fuel cells (LTFC), based on polymer electrolytes, depend on expensive catalysts sensitive to poisoning, thus needing high purity fuels. Intermediate temperature fuel cells (ITFC) appear as the ideal compromise between both systems.

Composites consisting of mixtures of ceramic oxide-ion conductors and alkaline carbonates are amongst the new types of electrolytes that may find application in LT/ITFCs. The high conductivities reached at around 500 °C exceed those typical of the best ceramic electrolytes at 800-1000 °C. One key feature of these electrolytes is a sharp increase in conductivity close to the carbonates melting temperature [1-2].

Published results suggested the possibility of fast ionic transport along the ceramic electrolyte/alkaline carbonate interface, enhanced in the presence of oxide nanoparticles. Also, ionic transport seems to be complex, including intrinsic (e.g., oxide and carbonate-ions) and extrinsic (protons) species [1-3].

This work presents an attempt to get further insight on the role of interfaces through the analysis of the electrical performance of several cells, including intimate mixtures of all constituents but also multilayer assemblies with well-defined interfaces.

Experimental

Disks of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) and mixtures (2:1, molar ratio) of Na_2CO_3 (NC) and Li_2CO_3 (LC) were prepared after pressing and shaping the individual constituents, followed by heating. Homogeneous composites involving high energy milling of all constituents (50 vol% of CGO + 50 vol% (NC+LC)), were also used as reference. All materials were firstly characterized by X-ray Diffraction (XRD) and Scanning Electronic Microscopy (SEM). Further experimental details can be found elsewhere [3].

Multilayer composite cells were also prepared superimposing alternate layers of the individual constituents (ceramic and carbonates). The volume percentage of each phase was kept as close as possible from the ratio adopted in the case of homogeneous composites. With final sintering around 500ºC, under light pressure, the ceramic/salt interfacial bonding was strong enough to tolerate grinding and polishing without delamination.

All cells were electroded with Au-paste for impedance spectroscopy measurements (20 Hz to 1 MHz range) in air, from 250 to around 600 °C. The layered cells performance was studied both as series or parallel association, after appropriate electroding.

Results and Discussion

Composites based on intimate mixtures of all constituents showed no detectable chemical interaction. Namely, the XRD pattern of these materials showed no shift in the position of the (fluorite) CGO peaks.
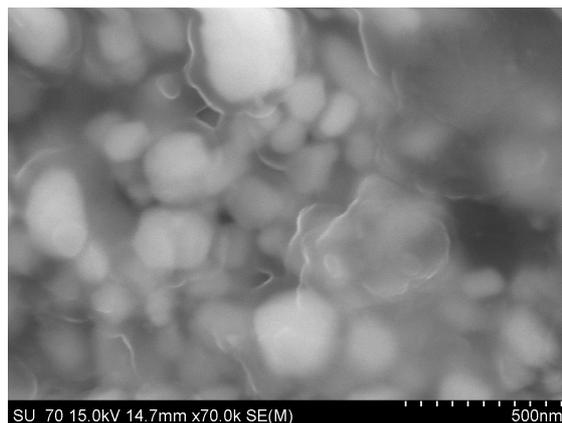

Fig. 1 Microstructure of one CGO-based homogeneous composite.

Figure 1 includes one typical microstructure of one homogeneous composite. The ceramic skeleton (white grains) is surrounded by the mixed carbonates phase (grey areas), and provides enough mechanical stability even at temperatures exceeding the carbonates melting temperature, around 500 °C. The grain size of the ceramic particles is clearly submicrometric, often nanosized. Percolation of the ceramic phase could be assumed in many cases, considering the already mentioned mechanical stability of the composite at high temperature.

The low temperature (below melting) impedance spectra of homogeneous composites usually consisted of one "bulk" high frequency contribution and one least defined low frequency electrode tail [3].

At high temperature the "bulk" response is not accessible anymore within the available frequency range (Figure 2). However, the electrode impedance arc is easily

seen and well defined, suggesting a minimum of two independent contributions (one large and depressed semicircle at lower frequency and one smaller arc at higher frequency). The high frequency intercept with the Z' axis of the electrode impedance arc corresponds to the "bulk" resistance.
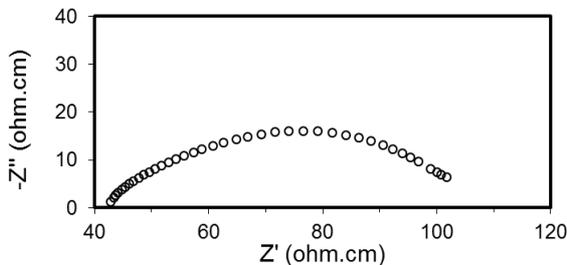

Fig. 2 Impedance spectra of one CGO-based homogeneous composite, in air, at 566 °C.

The shape and magnitude of the electrode arc shows that electroactive species involved in the ionic transport are easily available. This result is somewhat conflicting with the claimed dominant role of mixed carbonates. In fact, in molten alkaline carbonates ionic transport is due to the carbonate ion. Both carbon dioxide and oxygen are needed to form this species ($CO_2 + \frac{1}{2} O_2 + 2e^- = CO_3^{2-}$). In the absence of significant amounts of carbon dioxide in open air experiments, the absence of this species should have a visible consequence in terms of electrode impedance shape and magnitude. Modest electrode impedance suggests that other species are involved in the electrode process, namely water from ambient air humidity [3].
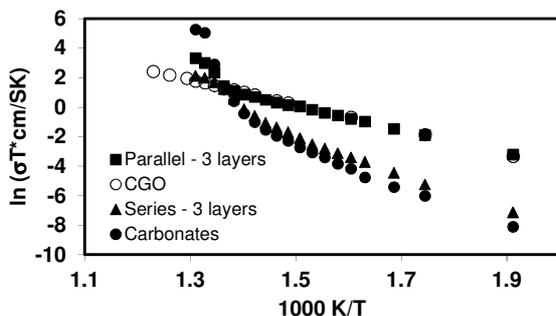

Fig. 3 Dependence of the total electrical conductivity on temperature for single phase CGO, mixed carbonates and parallel or series associations (see text for details).

In all multilayer assemblies the "bulk" cell resistance showed close agreement with common series or parallel association models (Figure 3). In the case of the series association, at low temperature the total cell resistance was dominated by the least conductive layers (carbonates). In the case of the parallel association, the cell overall resistance was governed by the best conducting phase (CGO). At temperatures above the carbonates

melting point, the carbonates become the best conductive phase and, again, the performance of the parallel and series associations are controlled by the best and worst conductors, respectively. The bulk electrical transport properties of these cells showed no obvious CGO/carbonates interfacial contribution.

Somewhat against this conclusion, the electrode impedances of parallel multilayer cell assemblies deviated considerably from those of individual components and approached those of homogeneous composites. The electrode response of these multilayer cells could be deconvoluted into two contributions, as already suggested in the case of Figure 2. This might be a fingerprint of relevance of multiple ionic species. In the case of homogeneous submicrometric or even nanocomposites the interfacial surface area between oxide and carbonates is orders of magnitude higher than in the case of layered cells. In such extreme microstructures we might be watching the same effects but combined in distinct proportions. This result suggests a trivial size effect instead of a true nanosize effect.

Qualitatively, the potential role of interfaces on the overall cell performance, namely in the cell/gas phase interaction, must also be considered. In fact, microsystems might develop locally at the surface favoring parallel reaction pathways and local equilibrium between gas phase and the corresponding ionic species in the composites.

Conclusions

Bulk ionic transport of multilayer cells could be described as simple associations of individual constituents, without any obvious interfacial effect. However, electrode impedances of all tested cells showed distinct and unique characteristics, raising the possibility of significant interfacial effects namely on surface reaction kinetics.

Acknowledgements

References

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