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Short communication

Redox behaviour of Gd-doped ceria–nickel oxide composites

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ABSTRACT

Reduction kinetics of NiO–gadolinium-doped ceria (GDC) composites was studied. NiO–GDC ceramic rods were fabricated by cold isostatic pressing of powders of nanometer size obtained by chemical synthesis. The rods were sintered in air at the maximum contraction temperature, 1350 °C, and treated in reducing atmosphere at different temperatures and reduction times. Progress of the reduction process was followed by the gravimetric method. By adjusting the data obtained from weight loss during the isothermal reduction at temperatures between 500 and 700 °C to standard diffusion models for a cylinder, it was possible to obtain effective diffusion coefficients for the material. The process activation energy was 0.9 ± 0.2 eV indicating that, in the whole temperature range studied, the reduction kinetics is controlled by the diffusion of O^{2-} throughout the ceramic matrix of GDC. SEM studies in reduced, partially reduced and completely reduced samples reveal a submicrometric microstructure with a uniform distribution of Ni phase surrounded by pores within ceramic GDC matrix. This microstructure is suitable for IT-SOFC anodes.

1. Introduction

In the last few decades, ceria materials doped with rare earths (Y^{3+}, Gd^{3+}, Sm^{3+}, etc.), especially gadolinia-doped ceria (GDC), have been proposed as electrolyte materials for intermediate temperature (500–700 °C) solid oxide fuel cell (IT-SOFC) [1]. Ceria-based materials are also being considered for the SOFC fuel electrodes because of the mixed ionic and electronic conductivity of reduced ceria [2]. Ceria-based anodes have some important advantages over conventional Ni-based anodes. For example, their ability to endure repetitive oxidation and reduction and the ability to avoid carbon deposition from hydrocarbon fuels. However, below 700 °C the electronic conductivity of doped ceria is not high enough to guarantee the cell current collection. A possible alternative would be to use ceria as the ceramic part in nickel porous cermet anodes (Ni–GDC). Beneficial effects of this strategy have been reported and interpreted as being probably due to the broadening of the three-phase boundary (TPB), that is, the zone where the electrochemical reaction takes place [3]. In addition, choice of GDC instead of for example Yttria stabilized Zirconia (YSZ) would result in better matching of the thermal expansion coefficients between the cermet Ni–GDC and the GDC electrolyte.

It is important to consider that the electrochemical performance of cermets depends largely on their microstructure. Cermet microstructure is a critical issue in the case of anode supported cells where the cermet is the structural component thus having thicknesses of several hundred microns [4]. The best electrochemical response of the anode material is for a uniform distribution of small Ni particles in the also uniform porous ceramic matrix. The chemical synthesis of the NiO–GDC powders, used in the present work, allows us to obtain nanometric powders with a uniform and homogeneous distribution of both phases. Using these powders we have been able to fabricate very homogeneous and fine grained NiO–GDC ceramics. Ni–GDC porous cermets are obtained by thermal treatment of NiO–GDC composites in reducing atmosphere (commonly by “in situ” reduction during the first cell start-up). During this process, the nickel oxide is converted into metallic nickel according to this reaction:

$$NiO_{(s)}\,(+GDC) + H_{2(g)} \rightarrow Ni_{(s)}\,(+GDC) + H_2O_{(g)}$$

Since the precursor oxide is confined inside a GDC matrix, the reduction in volume is converted into pores. Finally, in the cermet the GDC constitutes a three-dimensional matrix where Ni particles and pores are confined and the volume fraction of the phases is crucial in order to obtain good mobility of both the reacting species and the electrons. The microstructure is also important in order to inhibit Ni grain coalescence during the sintering process and at working temperatures.

Additionally, the study of the reaction mechanisms that take place during the reduction of NiO is very important since it allows us to define the best processing conditions to obtain a uniform distribution of fine metallic particles and pores within the cermet.

In recent years, the kinetics of the reduction of NiO to metallic Ni have been extensively studied in the conventional YSZ-based

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