

Cerium–terbium mixed oxides as potential materials for anodes in solid oxide fuel cells

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Abstract

Highly homogeneous (Ce,Tb) oxides are prepared by a microemulsion technique, and their structural and electronic state after high temperature calcination is examined with X-ray diffraction, high resolution transmission electron microscopy, X-ray photoelectron and absorption (XANES) spectroscopies and impedance spectroscopy measurements. Addition of Tb stabilizes significantly (in comparison to pure ceria) specific surface area and small particles sizes during high temperature calcination (up to 1100 °C); phase decomposition at these high temperatures, similar to that occurring when stabilization of ceria is carried out with Zr, does not occur, and the mixed oxide remains homogeneous throughout. Tb addition to ceria may thus be beneficial when used as a component of SOFC anodes. TEM data indicate reshaping of oxide particles and provide evidence of crystal superstructures after high temperature treatments, while XPS and XANES reveal an increase in the Tb⁴⁺/Tb³⁺ ratio (for a given pretreatment) with the Tb/Ce ratio; Ce seems to be less reducible to Ce³⁺ in the presence of Tb. Total electrical conductivity of CT samples under H₂ is mediated by electron transport (involving probably only Ce) and is lower than in gadolinia-doped ceria (GCO); in air conductivity is higher than for GCO, particularly at low temperatures, and it is probable that a p-type transport mechanism predominates in this case.

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1. Introduction

The use of ceria in Solid Oxide Fuel Cell (SOFC) anodes has received attention in recent years, particularly after the work by Park et al. [1], which shows its beneficial effect when the anode is fed directly with dry hydrocarbon as fuel; this is thought to be related to the known good characteristics of ceria as catalyst for the total oxidation of hydrocarbons. In these conditions of direct dry hydrocarbon feed, there is the problem that the Ni metal component used as electrical conductor in the anode composite promotes the formation of

carbon, which decreases the anode efficiency by blocking its pores. This has led some authors to propose the use in the anodes of copper, which is much less prone than nickel to promote carbon formation [2]. Copper has, however, the disadvantage of a lower melting point which leads to its gradual particle growth during cell operation, this being ultimately detrimental to the necessary electrical conduction. For this reason, Kim et al. [3] have proposed using a Ni–Cu alloy; this not only retards the metal particle growth but also gives rise to the formation of a small amount of carbon that, if adequately controlled, does not block pores and contributes to the required electronic conductivity; the amount of metal can, thus, also be lowered, allowing better control of particle size. This approach may require, however, a delicate control of material properties and process parameters to ensure that

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