

Design of composite anodes for IT SOFC based upon Ni/YSZ (ScSZ) cermet: effect of promoters on lattice oxygen mobility, reactivity and performance in CH₄ oxidation/reforming

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Introduction

For IT SOFC based on doped ceria or zirconia electrolyte, design of Ni-containing cermet anodes stable to coking and able to efficiently operate on methane feeds without excess of steam represents important but demanding problem still far from being successfully solved. A promising approach consists in doping of traditional cermets by complex oxides with a high lattice oxygen mobility [1-3]. This is expected to suppress coking due to more efficient activation of oxidant (water) and enhanced oxygen flux from the electrolyte to Ni surface. To increase the middle-temperature (600-700 °C) performance in the complete/partial oxidation of methane, small amounts of Pt group metals or Cu can be added. This work presents results of such research for the case of Ni/YSZ and Ni/ScSZ cermets.

Materials and Methods

Ni/YSZ and Ni/ScSZ cermets (Ni content up to 50%) were prepared from NiO and doped zirconia sources (either commercially available or prepared within this work by coprecipitation). They were modified by fluorite-like (Pr(2%)-Gd(18%)-Ce-O; Gd(20%)-Ce-O; Ce(50%)-Zr (50%)-O) and perovskite-like (La-Pr-Mn-Cr-O) complex oxides (up to 15 wt.%), along with precious metals (0.3 wt.% of Pt, Pd or Ru) or CuO (up to 10 wt.%). Oxide additives were mainly supported on NiO-doped zirconia composites by impregnation with water or methanol solutions of polymeric polyester citric acid-ethylene glycol precursors followed by drying and calcinations. As a new approach, one-pot synthesis of nanocomposites containing complex oxide promoters, NiO and dispersed doped zirconia particles has been carried out by mixing the polymeric precursors of all phases but solid electrolyte with calcined nanoparticles of the doped zirconia, burning this mixture and annealing it under air. Precious metals or CuO were supported by incipient wetness impregnation. Samples were characterized by XRD, TEM, specific surface and porosity measurements, H₂ and CH₄ TPR. Their catalytic properties in methane partial oxidation (PO) and steam reforming (SR) were studied in the 500-850 °C range in the flow reactor both in the isothermal and temperature-programmed modes for 0.5-1 mm samples fraction diluted by quartz. The amount and reactivity of the surface carbon accumulated under reaction conditions was estimated by using temperature-programmed oxidation (1% O₂ in He).

Results and Discussion

For undoped cermets, in stoichiometric feeds, SR starts only at temperatures exceeding 700 °C and is accompanied by the excessive carbon deposition leading to reactor plugging, which is more pronounced for composites containing ScSZ. Oxidic promoters suppress carbon deposition and increase the middle-temperature (~ 550 °C) performance. Pd, Ru, Pt or Cu addition further increases middle-temperature performance in stoichiometric feeds to the level sufficient for the practical application. The best performance in PO and SR was revealed for composites prepared via one-pot route due to a more uniform distribution of oxide promoters, electrolyte and NiO/Ni. Combination of platinum group metals with complex perovskites ensures a high and stable performance in the middle-temperature range in all studied feeds with excess or deficit of water, which makes them promising for the practical application (Fig. 1). A higher activity was obtained for samples without preliminary reduction before testing. Comparable though somewhat lower performance was found for copper-promoted samples (Fig. 1). Effect of the samples composition, microstructure and oxygen mobility on their catalytic activity was analyzed and used for their optimization.

Significance

Results of research are important for design of IT SOFC anodes operating on the natural gas

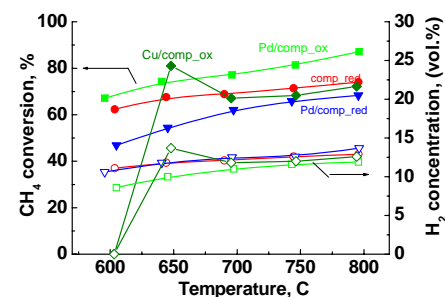


Figure 1. Temperature dependence of methane conversion and H₂ content in converted feed for La-Pr-Mn-Cr-O/ScCeSZ nanocomposites prepared via one-pot route and promoted by Pd (0.3 wt.%) or Cu (10 wt.%). Reaction mixture composition 8% CH₄ + 8% H₂O in N₂, 50 ms contact time. Samples pretreated either in O₂ (comp_ox) or H₂ (comp_red) (10% vol. O₂/H₂ in N₂) before testing.

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