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Combustion synthesis and characterisation of Ni-MO-YSZ ($M = Mg, Ca, Al_{2/3}$) cermet anodes for SOFCs

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Abstract

The performance of Ni-yttria-stabilised zirconia (YSZ) cermet anodes can deteriorate with time and on redox and thermal cycling due to coarsening and/or oxidation of the Ni particles. Small additions of a second oxide phase may arrest degradation. In this work, Ni-YSZ-MO compositions ($M = Mg, Ca, Al_{2/3}$, respectively, NZM, NZC, NZA) were prepared by combustion. Phase composition and microstructural characteristics were assessed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Powders calcined at 1450 °C consist of mixtures of Ni(Mg)O-YSZ, NiO-YSZ-$CaZrO_3$ and NiO-YSZ-$NiAl_2O_4$ particles for NZM, NZC and NZA, respectively. The sintered and reduced cermets are composed of a homogeneous and well-dispersed distribution of Ni, YSZ and secondary oxide components.

Keywords: Fuel cells; Powders-solid state reaction; Microstructure-final; Cermet anodes

1. Introduction

The most suitable material for a solid oxide fuel cell (SOFC) anode operating with hydrogen as fuel is a cermet containing Ni metal and an oxide-ion conducting ceramic phase, typically yttria-stabilised zirconia (YSZ).[1–3] The electrocatalytic and electrochemical performance of Ni-YSZ anodes can deteriorate as a result of oxidation or coarsening of the grains of the metal phase.[4] Some progress has been made recently in arresting degradation through the addition to the cermet of a tertiary phase. Incorporation of a second metal phase to form intermetallics or Ni alloys may improve oxidation resistance,[5] whereas small fractions of TiO_2 are reported to improve electrical conductivity and stability.[6] Tikekar et al.[7] recently studied the reduction and re-oxidation kinetics of Ni-YSZ cermets with small amounts of stable oxides (CaO, MgO, TiO_2) and report that the additives hinder reoxidation by inhibiting NiO-Ni particle shape changes during reduction-oxidation cycles. A more stable morphology leads to lower porosity and slower gas phase diffusion during oxidation.

Although the strategy of introducing an additional oxide appears to be promising, the effects of secondary oxide phase require more detailed examination, particularly in terms of phase composition, microstructure and the effects on stability. A further consideration, not to be analysed here, is the role the additional oxide may play in accelerating the electrode reaction kinetics.[6,8]

We have demonstrated that cermet anodes with submicron-scaled particles may be readily synthesised by combustion, giving polarisation resistances comparable to those of optimised electrodes prepared by more elaborate methods.[9,10] A particular advantage of combustion synthesis is that compositions with similar microstructures are routinely obtained. This allows a greater understanding of the role of compositional effects than is usually possible with processing techniques where differences in microstructure tend to mask compositional effects. In this work, Ni-YSZ cermet electrodes with a secondary oxide phase (Al_2O_3, MgO, CaO) are synthesised by combustion and assessed in terms of phase formation and microstructure.

2. Experimental procedure

The following nominal anode compositions were prepared by combustion synthesis: Ni-YSZ-MgO (NZM), Ni-YSZ-Al_2O_3

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(NZA) and Ni-YSZ-CaO (NZC), each with a content of 40 vol.% Ni, 50 vol.% YSZ and 10 vol.% of the secondary oxide, where YSZ denotes 8 mol.% yttria-stabilised zirconia.

The combustion-synthesis technique for the preparation of cermet anodes has been described previously.[11] Stoichiometric amounts of the component metal nitrates were mixed with urea in 100% excess; the mixture was melted on a hot plate and the temperature raised to ∼300 °C, upon which combustion took place. The as-obtained powder constituted an oxide mixture, which was subsequently pressed into disks and sintered at 1450 °C in air during 90 min. The high temperature is necessary for co-sintering the anode on YSZ electroyte.[11] Samples were annealed in a 10%H_2:90%N_2 atmosphere at temperatures between 700 and 1100 °C for several hours; the formation of metallic Ni was then assessed.

Phase analysis was performed on crushed and milled samples by XRD on Rigaku Geigerflex and Siemens D5000 diffractometers (both Cu Kα radiation). Microstructure was analysed by SEM, with a Hitachi S-1400 instrument equipped with RONTEC energy dispersive analysis (EDS), and TEM, using a 300 kV Hitachi H-9000, also equipped with EDS.

3. Results and discussion

The XRD patterns of the NiO-YSZ-MO combustion products sintered at 1450 °C in air are shown in Fig. 1. Ni(Mg)O-YSZ and NiO-YSZ-$NiAl_2O_4$ composites are formed for compositions NZA and NZM, respectively. In the case of the Ca-containing composition, a $CaZrO_3$-based perovskite forms. The relative intensities of the perovskite peaks suggest most of the Ca is present as the perovskite, although the slight shift of the fluorite peaks indicates that some calcia may be dissolved in the zirconia lattice. Solubility of Mg into ZrO_2 may also occur, but should be negligible as suggested by the fluorite lattice parameters and by TEM analysis, as discussed below. Small quantities of monoclinic zirconia ($mZrO_2$) detected for NZM and NZA (Fig. 1) suggest that the presence of secondary oxide phase may destabilise the cubic phase. It should be noted that $mZrO_2$ was not detected immediately after combustion. The fact that $mZrO_2$ is not observed for NZC may indicate that it has preferentially reacted with calcium to form the perovskite.

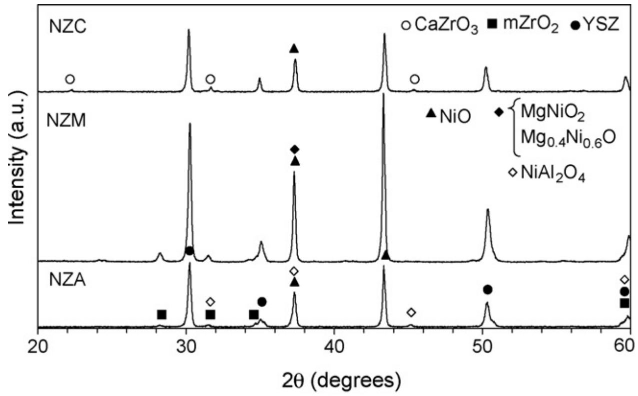

Fig. 1. XRD patterns of the cermet compositions sintered in air at 1450 °C.

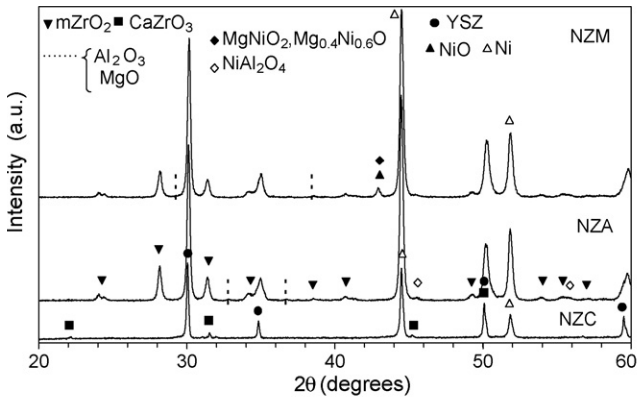

Fig. 2. XRD patterns of the cermet compositions sintered in air at 1450 °C and reduced at 800 °C for 7 h (NZC) or 1100 °C for 12 h (NZA and NZM).

Attempts to reduce the Ni-containing oxides were carried out by annealing in 10%H_2:90%N_2 at temperatures in the range 700–1100 °C. The corresponding XRD patterns of NZA and NZM reduced in H_2 at 1100 °C for 12 h, and NZC reduced in H_2 at 800 °C for 7 h, are shown in Fig. 2. The formation of Ni metal in NZM and NZA was observed only at 1100 °C, but the low intensity of the desired simple oxides, respectively, MgO and Al_2O_3, suggests that reduction may not be completed. A much lower annealing temperature (700 °C) was sufficient to fully reduce the NiO in NZC, but the stable $CaZrO_3$ perovskite remains. The significantly higher temperature required to reduce the Ni-containing binary oxides in NZA and NZM results from their higher stability with respect to NiO (reduced <700 °C).[11] However, some Ni forms at much lower temperatures in NZA (Ni peaks observed from 700 °C) than in NZM (from 1000 °C) due to the presence of both NiO and $NiAl_2O_4$. These XRD patterns also reveal an increase of the fraction of $mZrO_2$ with respect to the powders calcined at 1450 °C, probably as a result of reequilibrium at lower temperatures in such complex quaternary systems. It should be noted that commercial cubic-stabilised zirconias also contain a fraction of the monoclinic phase.

Typical scanning electron micrographs of the as-prepared combustion powders, and the sintered and reduced compositions are shown in Fig. 3. The general features of the combustion powders (Fig. 3a) are similar to Ni-YSZ and other cermet anodes prepared by this method,[8–11] consisting of agglomerates of variable size composed of submicrometric particles. The backscattered images shown for NZC and NZM (Fig. 3b and c) calcined at 1450 °C and annealed in H_2 at 700 °C reveal a homogenous mixture of two phases (note that NZM remains fully oxidised at 700 °C). The images demonstrate that calcining at 1450 °C does not excessively modify the microstructure, with both phases retaining a small grain size (micron range). Significant differences in chemical composition in NZC and NZM are apparent in the backscattered SEM micrographs. EDS analysis indicates that the grains of lighter tonality in NZC (Fig. 3b) are pure Ni. In NZM (Fig. 3c), however, Ni is identified as particles of darker tonality which, in backscattered mode, suggests the coexistence of Ni with lighter matter. These particles are likely to correspond to Ni(Mg)O, as observed in the XRD pattern of NZM. The effect of reduction on the cermet porosity is also

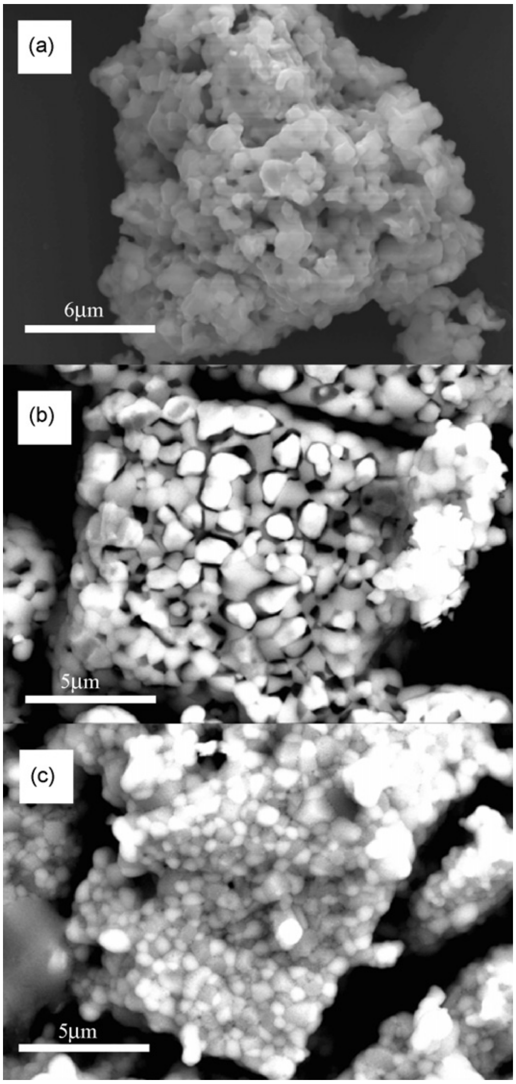

Fig. 3. Scanning electron micrographs of (a) as-prepared NZC, (b) NZC and (c) NZA, sintered at 1450 °C then reduced at 800 °C in H_2/N_2 (10:90).

noticeable. Whereas in NZC the fully reduced Ni particles are clearly separated from YSZ, the two phases in NZM form large, dense agglomerates with fewer pores.

The NZA cermets (not shown) share common features with both NZC and NZM. The NiO particles are easily reduced but the Ni_2AlO_4 spinel phase is reducible only at 1100 °C. Although the spinel was detected by XRD, SEM was of insufficient spatial resolution to characterise the particle distribution and morphology. TEM was, therefore, carried out in order to obtain a more precise analysis of particle composition. The bright field image shown in Fig. 4(a) shows $NiAl_2O_4$ particles isolated from NiO. The systematic analysis of NZM samples (Fig. 4b) did not reveal pure Ni particles, which suggests that the Ni(Mg)O solid solution is the only Ni-containing phase in the oxidised powders.

In terms of phase distribution, NZM could therefore be a favourable system for obtaining very fine grained Ni on full reduction, with the desired intimate mixture of Ni and MO. We note that for the three studied cermet compositions, the fine crystallites of Ni- and M-containing phases are clearly separated from the YSZ.

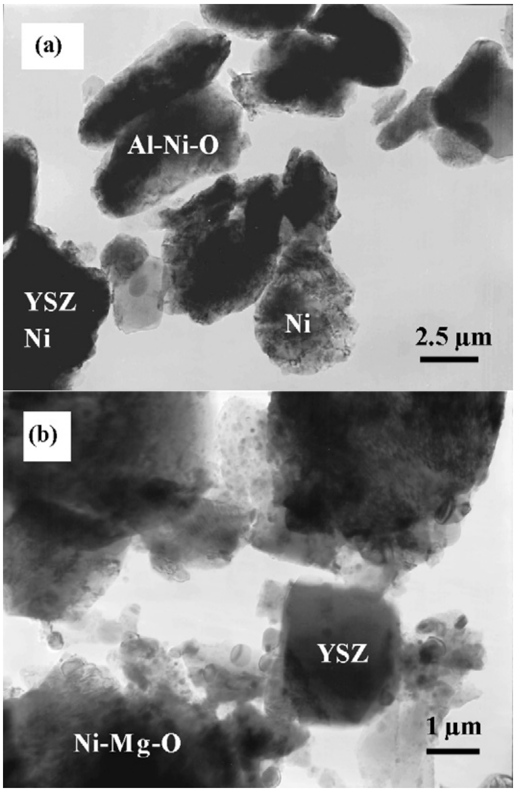

Fig. 4. Transmission electron micrographs of crushed pellets of (a) NZA and (b) NZC sintered at 1450 °C and annealed at 700 °C in H_2/N_2 (10:90).

The NZC composition may also merit further study due both to the potential influence of the refractory behaviour of $CaZrO_3$ on the anode cycling stability and the effect that the proton conduction exhibited by $CaZrO_3$-based phases may have on the reaction kinetics.[8] The latter property requires doping of the perovskite with a lower valence cation; however, we expect some Y to be dissolved on the Zr site during the combustion synthesis due to the similar atomic radii of Y and Zr.

4. Conclusions

Combustion-synthesised Ni-YSZ cermets with additions of MgO, CaO and Al_2O_3 consist of mixtures of Ni(Mg)O-YSZ, NiO-YSZ-$CaZrO_3$ and NiO-YSZ-$NiAl_2O_4$, respectively, in the as-prepared state. The sintered and reduced cermets are composed of Ni, YSZ and secondary oxide components (MgO, Al_2O_3 or $CaZrO_3$). In each case, the three phases are well-dispersed in a homogeneous matrix of high porosity. Ni-YSZ-MgO may be the most promising system for arresting anode degradation because of the very fine grained Ni obtained on reduction of Ni(Mg)O.

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