Journal of Power Sources 324 (2016) 679–686

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Synthesis, characterization and performance of robust poison-resistant ultrathin film yttria stabilized zirconia – nickel anodes for application in solid electrolyte fuel cells

F.J. Garcia-Garcia [a, *], F. Yubero [a], J.P. Espinós [a], A.R. González-Elipe [a], R.M. Lambert [a, b]

[a] Laboratory of Nanotechnology on Surfaces, Instituto de Ciencia de los Materiales de Sevilla (CSIC-Universidad de Sevilla), Avda. Américo Vespucio 49, 41092 Sevilla, Spain
[b] Chemistry Department, Cambridge University, Cambridge CB2 1EW, United Kingdom

HIGHLIGHTS

- Magnetron sputtering is very effective for fabrication of Ni-YSZ thin film anodes.
- Films deposited at oblique angles have enhanced porosity compared to typical cermets.
- They possess an extensive three phase boundary and thus high electrical conductivity.
- Addition of Au greatly increases resistance to poisoning by carbon deposition.

ARTICLE INFO

Article history:
Received 16 February 2016
Received in revised form
24 May 2016
Accepted 25 May 2016

Keywords:
Magnetron sputtering
Oblique angle deposition
Thin film anodes
Carbon-tolerant
SOFC

ABSTRACT

We report on the synthesis of undoped ~5 μm YSZ-Ni porous thin films prepared by reactive pulsed DC magnetron sputtering at an oblique angle of incidence. Pre-calcination of the amorphous unmodified precursor layers followed by reduction produces a film consisting of uniformly distributed tilted columnar aggregates having extensive three-phase boundaries and favorable gas diffusion characteristics. Similarly prepared films doped with 1.2 at.% Au are also porous and contain highly dispersed gold present as Ni-Au alloy particles whose surfaces are strongly enriched with Au. With hydrogen as fuel, the performance of the undoped thin film anodes is comparable to that of 10–20 times thicker typical commercial anodes. With a 1:1 steam/carbon feed, the un-doped anode cell current rapidly falls to zero after 60 h. In striking contrast, the initial performance of the Au-doped anode is much higher and remains unaffected after 170 h. Under deliberately harsh conditions the performance of the Au-doped anodes decreases progressively, almost certainly due to carbon deposition. Even so, the cell maintains some activity after 3 days operation in dramatic contrast with the un-doped anode, which stops working after only three hours of use. The implications and possible practical application of these findings are discussed.

1. Introduction

The potential of solid oxide fuel cells (SOFC) for clean, efficient power generation is widely recognized and has given rise to a very large body of research. One of the principal obstacles to large-scale implementation of SOFCs is that of limited anode lifetime caused by the severe operating conditions. The most widely used anodes are nickel-yttria stabilized zirconia cermets (YSZ-Ni) which are inexpensive and possess favorable electrical, catalytic and electrocatalytic properties, especially with respect to the use of hydrocarbon fuels, most notably methane. However, nickel is also very active for hydrocarbon cracking, leading eventually to gross carbon deposition, anode deactivation and mechanical failure. The subject has recently been reviewed in detail by Wang et al. [1] and very recently by Petrakopoulou et al. [2].

A variety of remediation strategies have been explored, including modification of the cermet's metallic and oxidic components, thermodynamic mitigation by means of internal steam reforming, and addition of a variety of dopants [1,2]. In regard to the

* Corresponding author.
E-mail address: fj.garcia@csic.es (F.J. Garcia-Garcia).

http://dx.doi.org/10.1016/j.jpowsour.2016.05.124
0378-7753/

latter approach, Gavrielatos et al. [3] showed that the performance of thick YSZ-Ni anodes prepared by a combustion method and operated in CH_4/steam could be significantly improved by addition of small amounts of Au. Their findings prompted the present work in which uniform, thermally robust, highly porous, un-doped and Au-doped YSZ-Ni thin film anodes were deposited on a YSZ electrolyte substrate by magnetron sputtering at an oblique angle of deposition (hereafter referred to as MS-OAD) [4]. We have previously demonstrated that this procedure yields porous columnar (as opposed to dense) anode films that are robust against morphological changes under thermal cycling in both oxidizing and reducing atmospheres, and which resist delamination from the underlying YSZ substrate [5]. Moreover, the MS-OAD method yields films with high and well-defined porosity [6–8]. This is an important asset in the present context in that such porous films have very extensive three-phase boundaries that maximize electrochemical performance in comparison to dense films produced by conventional normal incidence sputtering [9]. In regard to the synthesis of actual YSZ-Ni cermet anodes, both with and without Au doping, we show here that pre-calcination of the precursor films prior to reduction is critically important to the formation of well-structured homogeneous films. These two types of thin film anode were characterized in detail and then tested in a fuel cell fed with either hydrogen or methane + steam. The Au-doped (~1%) YSZ-Ni anodes exhibited far superior performance with respect to carbon deposition compared to their un-doped counterparts, due to formation of Ni-Au alloy nanoparticles whose surfaces were strongly Au-enriched. These poison-resistant Au-doped anodes are promising candidates for practical use as anodes in their own right. Moreover, as their thinness and porous morphology renders them robust against thermally-induced strain at the anode/YSZ electrolyte interface, they could also be used as highly conducting, stabilizing buffer layers between conventional functional anodes and the YSZ electrolyte; or as poison-resistant capping layers located on top of conventional thick film anodes.

2. Experimental: synthesis and characterization

Unmodified and Au-doped YSZ-Ni porous thin films were prepared by reactive pulsed DC magnetron sputtering using a power of 200 W, 80 kHz frequency and a working pressure of 5×10^{-3} mbar. Before deposition, the chamber was maintained at a base pressure of 3×10^{-6} mbar using as plasma gas a mixture of 40 sccm Ar and 2.5 sccm O_2. Commercially available solid oxide half-cells comprising electrolyte (YSZ) and cathode (20 mm Single Electrode Cell - Cathode Only, FuelCellMaterials, USA) were used as the substrates for electrochemical experiments performed with a commercial instrument (ProboStat, Norway). In these fuel cell experiments 100 sccm of pure H_2 or 10 sccm CH_4 + 90 sccm Ar + 10% steam was fed to the anode chamber and air was supplied to the cathode chamber at a flow rate of 100 sccm. Pt mesh was used as the current collector for both anode and cathode. An electrochemical workstation (AUTOLAB, PGSTAT30) with a four-probe configuration was used to obtain current–voltage (I–V) and current-power (I–P) characteristics at temperatures of 850 and 800 °C for H_2 and Ar + CH_4 + steam fuels respectively. Analysis of samples, deposited on a YSZ substrate, was by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), time-of-flight secondary ion mass spectrometry (TOF-SIMS), high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM), Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS). (For quantitative RBS analysis of the initially deposited films, silicon was used as substrate to ensure that Y and Zr signals were exclusively due to the thin film anode).

Oblique angle thin film deposition was carried out using two different targets: (i) a 50 mm diameter Ni/Zr/Y alloy (68.8/26.6/4.6 wt%) of 99.9% purity, chosen to produce YSZ films containing 8 mol % Y2O3 and 50 vol % Ni, and (ii) a similar target incorporating 3 Ni and 1 Au pellets in order to achieve Au doping of the films. The target-substrate distance was 5 cm with an angle of 80° between target and substrate normal and the deposition rate was 1.5 μm h^{-1}. A more detailed description of the deposition procedure may be found elsewhere [5]. Oblique angle deposition resulted in formation of highly porous anode thin films, crucial for achieving superior structural and electrical properties. The technique is very reproducible, straightforward, and well suited to scale-up, all sample preparations and analyses having been repeated at least twice [4,9].

The microstructure of films deposited on YSZ was examined by SEM using a Hitachi S4800 field emission microscope. RBS spectra were obtained in a tandem accelerator (Centro Nacional de Aceleradores, Universidad de Sevilla, Spain) with particle energy 1.557 MeV, beam current and diameter 1.7 nA and ~1 mm, respectively. The accumulated dose was 1.5 μC in all cases and spectra were analysed by means of the SIMRA6.0 program. XRD patterns were obtained using Cu Kα radiation with a Panalytical X'Pert Pro diffractometer incorporating a diffracted beam graphite monochromator and 1D silicon strip detector (X'Celerator). They were recorded from 2θ 10°–90° with step size 0.026° at 148 s per step. Analyses were performed using XPert HighScore Plus software. XPS spectra were recorded with a Phoibos 100 DLD (SPECS) instrument working with a constant pass energy of 20 eV. In accord with common practice, the binding energy (BE) scale is referenced to the C 1s peak (284.5 eV) arising from adventitious carbon. ToF-SIMS depth profiling analysis was performed on a ToF-SIMS type ION-TOF V instrument (Universidad de Extremadura, Spain), equipped with a Bipolyatomic primary ion source, a Cs/electron impact dual source column, and a low-energy electron flood gun for charge compensation of insulating samples. HAADF-STEM analysis was performed in a Tecnai20 high resolution TEM.

3. Results and discussion

3.1. Morphology and structure of YSZ-Ni anodes

Room temperature deposition produced anode precursor layers that contained poorly crystalline NiO and exhibited a typical tilted columnar microstructure resulting from shadowing effects during growth [4–8]. (The sharp YSZ peaks are due to the substrate). Reduction in Ar/5%H2 at 850 °C resulted in the morphology illustrated in Fig. 1 a,b characterized by marked surface segregation of large Ni particles (1.5–6 μm) along with smaller Ni particles (200–400 nm) interspersed within the YSZ nanocolumns. Other than the relatively large particles atop the film surface, the Ni particles were much smaller than those typical of YSZ-Ni anodes prepared by doctor blade or similar methods, which contain particles of up to 10 μm [10,11]. Clearly, decreased Ni particle sizes with narrow size distribution would improve the performance of such composite films as anodes in SOFC applications. Very substantial improvement can indeed be achieved, as shown below.

In marked contrast with the outcome of the H_2-only activation procedure, pre-calcination of the precursor layer in air at 1250 °C followed by reduction in Ar/5%H2 at 850 °C produced a very different morphology, illustrated in Fig. 1 c,d. This consisted of columnar aggregates (diameter ~ 800 nm) of composite material separated by ~ 80–140 nm channels and distributed uniformly across the film. The homogeneously dispersed small particles covering the entire external surfaces of the YSZ columns are attributed to Ni particles with a narrow size distribution. This structure should be well suited to the intended application because