Journal of Power Sources 193 (2009) 322–330

Contents lists available at ScienceDirect

Journal of Power Sources

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

Testing and improving the redox stability of Ni-based solid oxide fuel cells

M. Pihlatie[a,b,*], T. Ramos[a], A. Kaiser[a]

[a] Risoe National Laboratory for Sustainable Energy, Technical University of Denmark, P.O. Box 49, DK-4000 Roskilde, Denmark
[b] Helsinki University of Technology, Department of Engineering Physics, P.O. Box 4100, FI-02015 TKK, Finland

ARTICLE INFO

Article history:
Received 28 October 2008
Accepted 25 November 2008
Available online 13 December 2008

Keywords:
Fuel cells
SOFC
Redox stability
Ni-YSZ
Impedance spectroscopy

ABSTRACT

Despite active development, solid oxide fuel cells (SOFCs) based on Ni-YSZ anodes still suffer from thermomechanical instability under conditions where the anode side is exposed to oxidising conditions at high temperature. In the first part of the paper, structures and solutions, which could improve the redox stability of Ni-YSZ anode supported SOFC's in terms of dimensional and mechanical stability are reported. Porosity is identified as a major microstructural parameter linked to the dimensional and structural stability during redox cycling. The cumulative redox strain (CRS) after three isothermal redox cycles at 850 °C increases by a factor of more than 20 when the as-sintered porosity of the composites is reduced from 34 to 9%. The effect of reduction and redox cycling on the Ni-YSZ anode are discussed in light of electrochemical measurements using impedance spectroscopy on symmetric cells. When the symmetric cells are reduced and redox cycled isothermally at 850 °C, no major change in the serial or polarisation resistance of the cell and electrodes was measured. When the cells are, after the similar initial reduction treatment, redox cycled at 650 °C, the serial resistance remains almost unchanged but the polarisation resistance decreased by about 60%.

1. Introduction

Solid oxide fuel cells (SOFCs) continue to be a promising energy conversion technology for environmentally benign power generation, capable of utilising different hydrocarbons as well as hydrogen as the fuel [1]. Despite active search for alternatives such as fully ceramic or nickel-free anodes, Ni-YSZ composites are still widely used fuel electrodes [2–4]. Such cermets often also serve as structural materials for the electrochemical devices, either in planar or tubular designs. A generally known drawback of the Ni-based cells is that they are susceptible to thermomechanical instability when the anode side is exposed to oxidising conditions at high temperature. While many of the fundamental degradation mechanisms of the SOFC are currently known and strategies exist on how to overcome them, the problem of redox stability remains as a one of the cumbersome tasks [5]. Oxidation of the Ni contained within the porous composite into NiO entails a substantial volumetric expansion that exerts large stresses on the ceramic backbone of the composite. The re-oxidation of an operating cell can lead to mechanical rupture, leaks, and in the worst case a catastrophic failure of the SOFC. The solutions to the redox stability problem of SOFC can be approached at many levels: with SOFC system control and design, by design of cell and stack geometry, or through materials selection as well as optimisation of the microstructure and composition of the anode half cell. The optimal and most cost effective way to design the cell, the stack and the system depends on several factors such as system size, typical or required load profiles and the level of safety and automation systems. For example, elaborate safety or purge gas systems may not be affordable in small scale systems and therefore the durability of the cell itself plays a central role. To circumvent the redox stability problems in practical SOFC systems, the optimal solution is to have a system composed of robust, redox stable cells that can withstand partial or even full re-oxidation without significant losses to their functionality.

Different strategies to mitigate the redox instability at cell level, that is, of a single repeating unit (SRU), comprise geometrical design of the cell, materials selection and microstructural design of the structural components. Geometrically, both the “1st generation” thick electrolyte supported cell and the micro-tubular SOFC are more robust to thermal or redox cycling as compared to the thin electrolyte anode supported cell [6–9]. On anode supported electrolyte (ASE) SOFC, Wood et al. discussed different approaches to improve redox stability [10]. On the selection of materials, novel compositions such as fully ceramic Ni-free anodes, e.g. [11], are being developed, but their technological viability in terms of reproducibility, durability and cost remains to be proven. The redox properties of an ASE cell based on Ni-YSZ can be tackled through processing by variations in microstructure and composition. The impact of microstructure on the stability of Ni-YSZ cermets has been addressed in thermomechanical, dimensional and kinetics studies.

---

* Corresponding author. Present address: VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Finland. Tel.: +358 45 1103464/400 430395; fax: +358 20 7227048.
E-mail addresses: mikko.pihlatie@iki.fi, mikko.pihlatie@vtt.fi (M. Pihlatie).

0378-7753/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jpowsour.2008.11.140

Both Itoh et al. and Waldbillig et al. report that they have found more stable structures when implementing composites with coarser particles [12,13]. Even though the coarser phase for Itoh et al. was zirconia and for Waldbillig it was Ni/NiO, the basic effect of this modification is likely to be the same, that is, to slightly increase the porosity of the sample. Waldbillig et al. state the anticipated positive effect to redox stability from slightly reducing the Ni content; at the same time it must be ensured that sufficient Ni percolation remains [14]. It has been established by mechanical modelling that the ASE can withstand about 0.1–0.2% expansion of the supporting composite during redox cycling without cracking [7,15,16]. This level of dimensional stability of the supporting composite thus constitutes a suitable target level, which could enable an intact cell after a redox cycle without resorting to additional tricks such as functionally graded structures [14] or novel but more labour consuming manufacturing techniques like Ni infiltration [17].

Waldbillig et al. [14] investigated the effect from two functionally graded modifications: a twin-layered graded anode having less nickel in the layer next to the electrolyte to alleviate stress concentration, and a more dense (air) diffusion barrier layer at the backside of the anode support to slow down re-oxidation kinetics. The authors reported that both of these variations improved redox tolerance by reducing the electrochemical performance loss of the cell. Busawon et al. [17] report dimensional stability and fair electrical conductivity on pre-sintered porous YSZ backbones where 12–16 wt.% Ni was infiltrated into the YSZ structure. The challenge with this kind of approach is whether or not suitable and cost-effective techniques can be found for up-scaled production. Sarantaridis et al. [18] have shown the importance of the oxidation procedures for the thermomechanical behaviour and failure modes of the ASE cells. While the investigated cells could tolerate a Degree of Oxidation (DoO) of about 50% when exposed to air from the backside (anode side flow channels), an electrochemically driven oxidation by oxygen arriving across the electrolyte resulted in cell failure already at a DoO of about 5%. Therefore, the results indicate that a local (fast) oxidation in the anode–electrolyte interface where the anode is relatively dense is the worst operation mode of the cell and generates a stress peak at the electrolyte. This type of situation might arise e.g. on extreme cell loading with fuel utilisation approaching 100% when the local $p(O_2)$ could approach or exceed that needed for oxidation of Ni or, to a lesser extent, through fast communication of oxygen through the backside of the anode support to a more dense anode in a design where the anode support is very porous.

Besides the thermomechanical degradation and failure due to redox cycling of Ni-based ASE cells, the electrical and electrochemical effects are naturally of interest. The thermomechanical degradation of the Ni-YSZ cermet, detachment of the anode/electrolyte interface and failure of the electrolyte result in loss of electrochemical reaction sites, ionic conduction paths as well as loss of fuel, generally observed as performance loss of the cell. In many occasions, especially on full re-oxidation, the integrity of the ASE is lost so that the performance of the anode after the redox cycle is impossible to assess. The DC electrical conductivity of Ni-YSZ composites with coarse Ni has been reported to increase from 500 to 1000 S cm^{-1} upon a redox cycle at 850 °C by Grahl-Madsen et al. (the in-plane conductivity also given at 850 °C) [19]. Young et al. report an increase in DC electrical conductivity of Ni-YSZ anode support cermets as a function of redox cycles at 800 °C, whereas the conductivity in an anode composite, presumably having another microstructure decreased. The electrochemical performance of the anode improved on redox cycling at 800 °C for both the serial and polarisation resistance, as long as the ceramic backbone and the electrolyte remained intact [20].

The redox instability mechanism due to the sintering of nickel has been discussed by Klemensø et al. [21]. It has been demonstrated that the dimensional stability on redox cycling is very dependent on the conditions under which the reduction and re-oxidation takes place. The main operation conditions affecting redox stability are temperature and humidity. Both of them affect the growth of Ni particles in the reduced state through particle coalescence and sintering. In addition to Ni sintering, the temperature of re-oxidation plays a significant role for the dimensional behaviour in that re-oxidation at high temperature (850 °C or above) leads to larger redox expansion [22,23]. Additionally, the dimensional changes and the resulting thermomechanical behaviour depend closely on the composite microstructure as will be shown in the present paper. While the supporting composite can be optimised for structural and dimensional stability, electrical conduction and gas transport, the anode itself has less free microstructural parameters to be modified since it should retain its good electrochemical performance. Therefore, we deem it justified to pursue examining both the dependence of the cermet dimensional response on some microstructural variations, and the effect of redox cycling as well as the temperature of redox cycling on the electrochemical performance of the anode with a typical microstructure. This paper addresses thermal analysis, including dimensional behaviour from dilatometry and reduction–oxidation kinetics from thermogravimetric analysis (TGA), of a few different processing variants of Ni-YSZ composites. The second part of the paper assesses the electrochemical performance and microstructure of symmetric cells with Ni-ScYSZ anodes, before and after redox cycling at different temperatures. In a related work, we plan to implement modified ASE cells and test them for redox stability in comparison with standard cells.

2. Experimental

2.1. Ni-YSZ cermets

The cermets tested were manufactured from commercial NiO and 3YSZ powders using standard ceramic processing techniques and equipment. The powders were ball milled in ethanol-based slurries using dispersants and organic binders. The green tapes were cut into a number of sibling pieces for use in either TGA or dilatometry, and sintered at 1300–1400 °C. The as-sintered sizes of the dilatometry samples were about 5 mm × 24 mm, while the TGA samples were about 5 mm × 15 mm with a Ø2.5 mm hole in one end. The thickness of the tested samples varied, depending on the thickness of the tape cast, between 0.3 and 0.8 mm. The baseline samples were similar to those reported in [22,23]. Different modified composites were prepared using the same ceramic processing route and by varying the particle size distributions of NiO and YSZ. The size distributions of powders were measured using a Beckman Coulter laser diffraction instrument. Table 1 shows the available open and total porosities of the samples. The open porosities were measured by mercury intrusion porosimetry using a Micromeritics instrument. The total porosities were determined by geometrical measurements for larger samples as described in [24]. The total porosities in the reduced state of the baseline samples are about 35–40%, for sample A about 29% and for the modified samples D–N up to about 52%. Different variants of the industrial grade NiO powder used comprised pre-milled uncalcined, calcined, and powder doped with secondary oxides of either Mg, Al or Ce. The secondary oxide coatings were implemented through application of oxide precursors during ceramic processing. It should be stressed that there are several overlapping processing parameters fundamentally affecting the as-sintered microstructure, porosity and subsequent redox stability of the composites. These parameters include the sintering time and temperature, the particle size distributions of the powders and the sintering characteristics of each powder or raw