



Ion transfer in Ni-containing composite anodes of solid oxide fuel cells: A microstructural study

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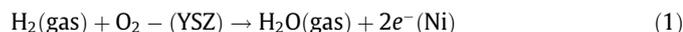
ABSTRACT

High-resolution transmission and scanning electron microscopy of the solid oxide fuel cell (SOFC) anodes made of Ni and yttria-stabilized zirconia (YSZ), revealed a substantial microstructural reconstruction induced by the anodic current. These microstructural alterations, primarily the growth of NiO inclusions at the Ni | YSZ interface, the resultant orientation relationship between the NiO and YSZ grains, and Ni grain fragmentation on subsequent reduction, provide a straightforward evidence for the so-called oxygen spillover mechanism of the anodic reaction.

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1. Introduction

In-depth analysis of the microscopic mechanisms determining electrode reaction kinetics in solid oxide fuel cells (SOFCs) has a key importance for developments of high-efficiency power generators and related technologies [1,2]. During the last decades, numerous works were focused on these mechanisms and, in particular, on the anode processes in SOFCs [1,3–20]. Even in the relatively simple case of hydrogen oxidation on the standard composite anodes comprising metallic Ni and yttria-stabilized zirconia (YSZ):



The overall reaction rate may be limited by, at least, three different processes: (i) charge transfer, (ii) surface electrochemical or chemical reaction, (iii) transport in the gaseous phase. There exist two general mechanisms, which are still the subject of debates. One of them, so-called hydrogen spillover mechanism, was considered as rate-determining by numerous researchers [13–16]. This mechanism involves molecular hydrogen dissociation at the Ni surface, proton transfer across nickel grain bulk [13–15] or surface [16] to the YSZ solid electrolyte, and recombination of these protons with oxygen anions from YSZ forming water on the electrolyte surface. Up to now, no direct experimental evidences of this mechanism were reported. Another well-known mechanism based on the

oxygen spillover [17–20] involves oxygen anion migration from YSZ to nickel and its subsequent reaction with hydrogen.

The present work was centered on the studies of microstructural and chemical changes that occur in the composite anodes during SOFC operation. In order to obtain supporting evidences for one or another mechanism of the anodic reaction, specific microstructural features of standard Ni-YSZ anodes were analyzed prior to and after SOFC testing. The results of high-resolution transmission electron microscopy (HRTEM) give additional arguments in favor of the oxygen spillover mechanism.

2. Materials and methods

Ceramic solid-electrolyte membranes with the thickness of 500 μm and diameter of 20 mm, made of 8 mol.% yttria co-stabilized zirconia (YSZ, FuelCellMaterials, USA), were used for model SOFC manufacturing. The cermet double-layer anodes were made of Ni and YSZ. The functional anode sublayer deposited onto the electrolyte by screen-printing, consisted of reduced NiO/YSZ (40:60 wt%) mixture. The current-collecting layer was screen-printed onto the top of the functional layer using a paste containing NiO and YSZ mixture (60:40 wt%) with additions of rice starch pore former and an organic thinner (mass ratio of 2:1). The cathodes were made of lanthanum-strontium manganite (LSM) deposited onto a protective interlayer of Gd_{0.1}Ce_{0.9}O_{1.95} (GDC). All the layers were deposited by an Ekra E2 screen-printer (Asys, Germany) using pastes with Heraeus V006A thinner. The electrochemical measurements were carried out by a 2-electrode technique using a Solartron

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1260A precision impedance analyzer and a Solartron 1287 potentiostat-galvanostat. During testing the fuel, namely humidified H_2/N_2 gas mixtures with variable hydrogen content fixed by Bronkhorst mass-flow controllers, was continuously supplied into the anode chamber. The oxidant supplied onto the cathode was dry synthetic air. The microstructure prior to and after electrochemical tests were studied by scanning and transmission electron

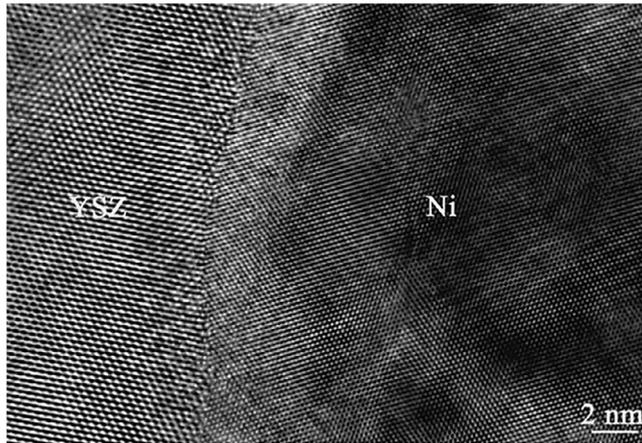


Fig. 1. HRTEM image of the boundary between YSZ and metallic Ni in the as-prepared cermet anode reduced in hydrogen at 800 °C.

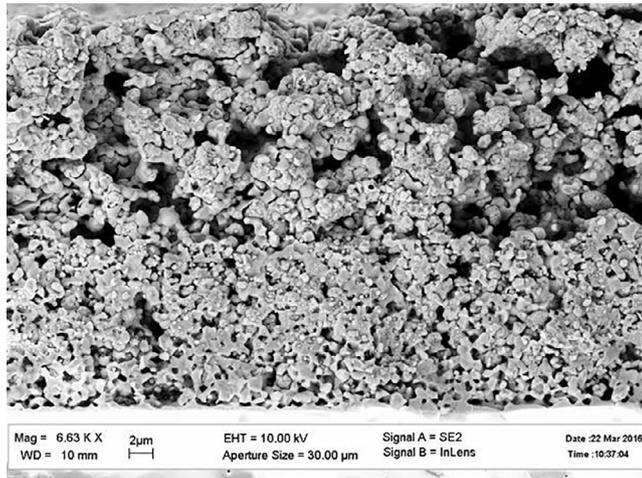


Fig. 2. SEM micrograph of the cross-section of two-layer composite anode after long-term SOFC testing.

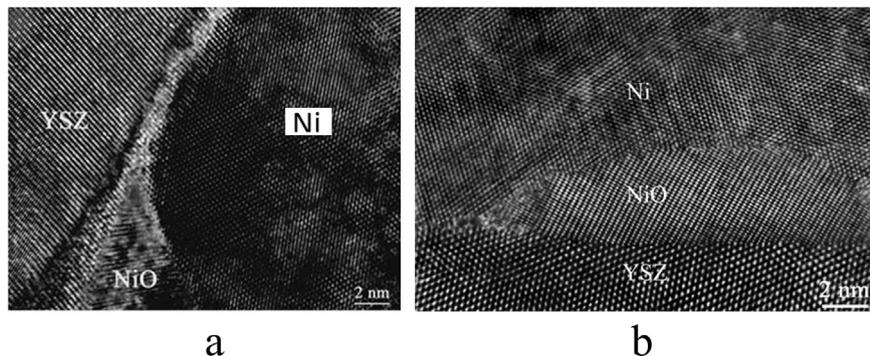
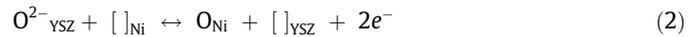


Fig. 3. HRTEM images of the boundary between YSZ and NiO nano-grains formed during SOFC operation.

microscopy (SEM/TEM) using Zeiss-Supra-50VP (Germany) and JEOL 2010F (Japan) microscopes, respectively.

3. Results and discussion

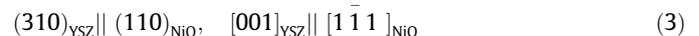
For the oxygen spillover mechanism, an elementary charge-transfer step at the composite anode can be considered as the transfer of one oxygen anion from solid-electrolyte surface to the surface of electronically conducting Ni [21]:



As a result, an adsorbed oxygen atom appears at the nickel surface and then interacts with molecular hydrogen diffusing from the gaseous phase; two electrons are passed to the external circuit via the three-dimensional network of Ni grains. Note that, as the presence of chemisorbed oxygen at the Ni surface is equivalent to an initial stage of nickel oxidation process, one can expect an appearance of nano-scale NiO inclusions or grains when oxygen flows are moderate.

Consequently, the morphology of interfacial regions between stabilized zirconia and Ni prior to and after passing direct current (DC, up to 300 mA/cm²) in SOFC was studied by high-resolution transmission and scanning electron microscopy (HRTEM/SEM). One HRTEM image of such a boundary, collected after reduction of the Ni-YSZ anode in flowing hydrogen at 800 °C under open-circuit conditions, is presented in Fig. 1. A good adhesion between the oxide and metallic phases results in an excellent, dense contact formed on sintering.

After SOFC operation, the anode microstructure showed substantial alterations, including a fragmentation of nickel grains and morphological changes of the boundaries between YSZ and Ni. The size and distribution of the YSZ grains remain essentially unchanged. An illustration of these effects at the micron-scale is presented in Fig. 2. At the nano-scale level, the formation of small NiO inclusions in the near-boundary regions of nickel grains was observed, primarily at the Ni|YSZ interfaces (Fig. 3a,b). In addition, the high-resolution electron microscopy studies demonstrated a preferred orientation relationship between the fluorite-type YSZ lattice and the nano-sized NiO inclusions formed under DC conditions:



This indicates that the NiO nano-grains were nucleated on the surface of YSZ as the substrate. The local epitaxial growth of NiO on the YSZ surface may only occur due to oxygen spillover from stabilized zirconia to metallic nickel.

The observed size of NiO grains, 100–200 nm, is in a good agreement with oxygen diffusion coefficient in nickel. The level of the oxygen diffusion coefficients reported in numerous works

(e.g., [22]) is close to 10^{-9} cm²/s at 800 °C. This gives the oxygen diffusion depths in Ni grains up to 200–300 nm even for a short diffusion time, such as 1 s.

The nano-sized NiO formed due to anion transport participates in the hydrogen oxidation on the anode:



The fragmentation of nickel grains in the vicinity of their contact with the solid electrolyte originates, therefore, from the reverse reduction of NiO back into metal. These results provide an evidence of two-stage mechanism of the hydrogen oxidation reaction on the cermet Ni-YSZ anodes:

- i. $\text{O}^{2-}(\text{YSZ}) + \text{Ni} \rightarrow \text{NiO} + 2\text{e}^-$
- ii. $\text{NiO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{Ni}$

where all anions are supplied into the reaction zone via the anion-conducting phase.

4. Conclusions

High-resolution electron microscopy studies of the SOFC anodes made of standard Ni-YSZ cermets, revealed substantial microstructural alterations induced by the anodic current. At the micron-scale level, these alterations include a fragmentation of Ni grains, whilst the sintered YSZ matrix remains essentially unchanged. The fragmentation originates from an appearance and growth of NiO nano-grains in the interfacial regions between YSZ and Ni, and their subsequent reduction when the current decreases. The orientation relationship between YSZ and nanosized NiO indicates epitaxial growth of nickel oxide on the YSZ surface as the substrate, which may only be possible due to oxygen anion transfer from YSZ onto the metal surface. These findings provide a strong argument in favor of the so-called oxygen spillover mechanism of the charge transfer when hydrogen is oxidized on the composite Ni-YSZ anodes.

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