Effect of Water Vapor Amount in a Hydrogenous Atmosphere on Structure and Properties of Nickel-Zirconia Anode Materials for Solid Oxide Fuel Cells

Bogdan Vasyliv, Viktoriya Podhurska, Orest Ostash
Karpenko Physico-Mechanical Institute, 5 Naukova str., Lviv 79060, Ukraine
E-mail: vasyliv@ipm.lviv.ua

Abstract: Nickel-zirconia anode ceramics of YSZ–NiO system for solid oxide fuel cells (SOFCs) has been investigated. A series of specimens were singly reduced in hydrogenous atmosphere (the Ar–5 vol%H_2 mixture) at 600°C under the pressure of 0.15 MPa or subjected to reduction-oxidation (redox) cyclic treatment at 600°C. Influence of water vapor concentration in hydrogenous atmosphere on structure and properties of the materials was studied. Based on structural changes in the as-received material it was revealed that a small amount of water vapor in Ar–5 vol% H_2 mixture (water vapor pressure below 0.03 MPa) accelerates a reduction of the nickel phase at 600°C with formation of nanopores on tiny Ni particles. A higher concentration of water vapor (the pressure above 0.03–0.05 MPa) causes a converse change in the reduction kinetics. For as-received material, such an amount of water vapor in the mixture is an obstacle for its reduction. For the material treated by redox cycling, better physical and mechanical properties were revealed after dwelling at 600°C in a water depleted gas mixture. Based on the SEM microscopy and the data on the conductivity and strength, the dual effect of water vapor on durability of a nickel-zirconia anode is discussed.

Keywords: SOFC anode material; hydrogenous atmosphere; water vapor.

1. Introduction

In order to apply the best preconditioning mode for the YSZ–NiO anode ceramics, a suitable range of treatment temperatures is to be revealed. It is known that temperatures within the 550-600°C range are the most effective for the reduction of NiO powders [1]. However, exposition of NiO ceramics in Ar–5 vol%H_2 mixture, that can be used for gradual reduction of SOFC anodes, for 4 hours at 600°C causes partial reduction of the NiO particles forming thin edgings of metallic Ni (of thickness of 0.1–0.3 μm) around them [2]. During redox treatment of NiO ceramics, structural transformation of boundaries of contacting nickel phase particles occurs causing increase in strength.

It was revealed for ScCeSZ–NiO anode ceramics that at certain redox treatment regimes substantial improvements in strength (up to 112%) and electrical conductivity can be reached [3]. It was also found that after the redox treatment of YSZ–NiO anode ceramics at certain regimes improvements in physical and mechanical properties occur [4, 5].

The efficiency of the fuel cell is known to rely significantly on fuel gas composition. It is known that the electrochemical oxidation of H_2 is strongly influenced by the steam content in the fuel. It has been reported that a small amount of water (few %) significantly helps decrease anode polarization resistance, while too large an amount of water can degrade anode performance, especially at high electrical load and low concentrations of H_2 in the fuel [6]. The mechanism by which the steam content in fuels promotes the H_2 oxidation reaction is still not well established. There is contradictory evidence as to whether adsorption of oxygen species from water on the ceramic part of a cermet anode or the metal part of the anode plays the key role in promoting the reaction.

It has been observed [7] redistribution of Ni in the YSZ–Ni cermet after prolonged operation at high water vapor pressures under current load, with formation of clusters and particles of Ni on the electrolyte surface next to well-defined Ni/YSZ contacts. This has been explained by formation of $Ni(OH)_2$ (gas) with a considerable vapor pressure under anodic operation in the presence of high water vapor pressures. It is not unlikely that large local concentrations of water and following concentration gradients may be able to remove Ni from the triple phase boundary and deposit it on a nearby surface as the water vapor pressure decreases. NiO is also known to diffuse out on a YSZ surface under oxidizing conditions, and the solubility of NiO in YSZ may contribute to the formation of Ni clusters on the YSZ surface in reducing atmosphere.

The aims of this work is to study an effect of water vapor amount in a hydrogenous atmosphere on structure and physical and mechanical properties of YSZ–Ni anode materials for solid oxide fuel cells after various kinds of preconditioning, and also to find out microstructural changes causing resulting properties of the material.

2. Material and methods

Anode ceramics of YSZ–NiO system sintered of zirconium oxide powder stabilized with 8 mol% Y_2O_3, with the addition of 50 wt% NiO, has been investigated. A series of specimens of the size of 1×5×25 mm were subjected to one-time reduction in hydrogenous atmosphere (the Ar–5 vol%H_2 mixture) for 4 hours at 600°C under the pressure of 0.15 MPa, or to 'reduction in the mixture – oxidation in air' (redox) cycling at 600°C according to [5, 8] (see Table 1). The preconditioned specimens and the as-received ones were then subjected to the dwell for 4 hours in 'water vapor – the Ar–5 vol% H_2 mixture' atmosphere at 600°C under the pressure of 0.15 MPa. In order to reach the pressure of 0.15 MPa, the test chamber was degassed and filled with water vapor of a certain pressure (0.03 or 0.148 MPa), and then filled up to the pressure of 0.15 MPa with the Ar–5 vol%H_2 mixture. The test conditions were divided into three modes, and the names of samples contained designations of preconditioning and treatment modes (see Table 1).

Table 1. The treatment regimes for the materials tested

Name of a series	Preconditioning	Test mode
A1	A	1
R1	R	1
RO1	RO	1
A2	A	2
R2	R	2
RO2	RO	2
A3	A	3
R3	R	3
RO3	RO	3

A – as-received material, R – one-time reduction in the Ar–5 vol% H_2 mixture for 4 hours at 600°C under the pressure of 0.15 MPa, RO – redox treatment for 5 cycles (reduction in the Ar–5 vol% H_2 mixture – oxidation in air), mode 1 – no treatment, mode 2 – dwelling for 4 hours in 'water vapor – the Ar–5 vol% H_2 mixture' atmosphere at 600°C under the pressure of 0.15 MPa (water vapor pressure 0.03 MPa), mode 3 – dwelling for 4 hours in 'water vapor – the Ar–5 vol% H_2 mixture' atmosphere at 600°C under the pressure of 0.15 MPa (water vapor pressure 0.148 MPa).

Ultimate fracture stresses of materials in the initial state, σ_{f0}, and after corresponding treatment, σ_f, were determined during the three-point bending test of the specimens in air at 20°C. Based on these data relative strength, σ_f / σ_{f0}, of the material treated was evaluated.

Specific electrical conductivity of material, σ, was determined in air at 20°C using the Van der Pauw method [9]. Fracture surface morphology of specimens was studied using SEM with secondary electron images. For this purpose the electron microscope Carl Zeiss EVO-40XVP was used.

3. Results and discussion

It is known [2, 8] that exposition of YSZ–NiO ceramics at the temperature 600°C for 4 hours in the Ar–5 vol%H_2 mixture causes formation of thin Ni edgings around NiO particles. As compared to as-received material residual stresses have not changed, and no noticeable change of zirconia skeleton has been found. But reduction in strength to 84% of the value for the as-received YSZ–NiO ceramics, caused by partial structural transformation of nickel phase, has been found for this mode of the treatment. The network of united Ni shells allows the electrical conductivity to be satisfactory. In pure hydrogen, nanopores on Ni particles formed due to their shrinkage as well as the pores between the particles prevent the rise of residual tensile stresses, but the nickel phase transformation followed by volume change and formation of pores causes the loss of a significant percentage of particle bonds and violate material integrity. Thus, reduction in strength to 48% of the value for the as-received YSZ–NiO ceramics was found.

Taking into account the mentioned peculiarities, we used in this work the Ar–5 vol%H_2 mixture for gradual reduction of SOFC anode material.

A strong tendency to increase the strength of material after both the one-time and redox preconditioning has been observed (mode 1 in Fig. 1a, b). Electrical conductivity of material has increased to a quite appropriate level as a result of reduction of a nickel phase (mode 1 in Fig. 1c). In particular, slight advantage in electrical conductivity is observed for the material after one-time reduction in the Ar–5 vol% H_2 mixture for 4 hours at 600°C under the pressure of 0.15 MPa (R1 series) as compared to one redox treated for 5 cycles (reduction in the Ar–5 vol% H_2 mixture – oxidation in air) (RO series).

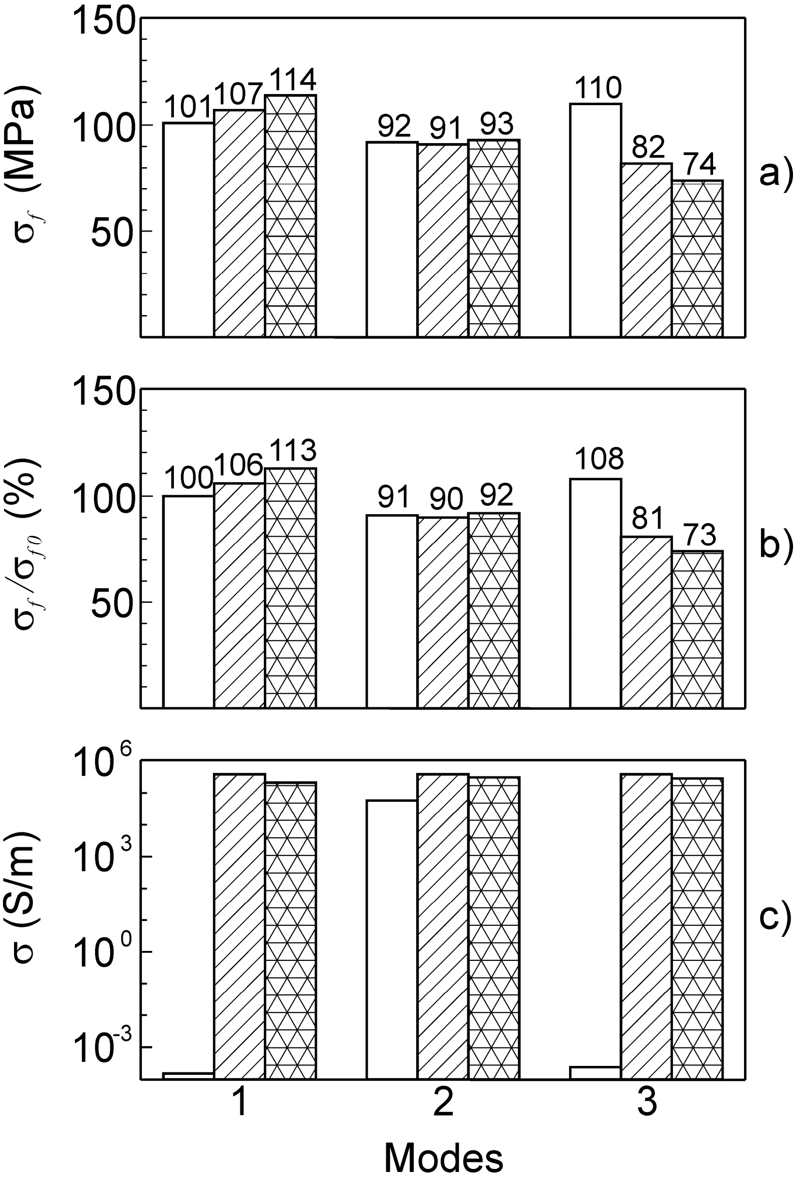

Fig. 1. Ultimate fracture stresses, σ_f, (a), relative strength, σ_f/σ_{f0}, (b), and specific electrical conductivity, σ, (c) for materials tested in modes 1–3 (see Table 1);
white bars – A series (no preconditioning); hatched bars – R series (preconditioning by one-time reduction); cross-hatched bars – RO series (preconditioning by redox cycling); numbers above the bars indicate values of corresponding parameters

At low magnifications we observed flat surface morphology of a specimen in A series (Fig. 2a). It corresponds to a good quality of sintering YSZ–NiO ceramics. A coarse agglomerate fracture was observed for R series (Fig. 2c) and especially for RO series (Fig. 2e) contrary to the fracture for A series. This explains a strength increase following the growth of fracture surface area.

At high magnifications we can observe signs of ductile elongation of the nickel phase particles for R series (Fig. 2d) and especially for RO series (Fig. 2f). Contrary to this, brittle debonding of the NiO and YSZ particles is observed for A series (Fig. 2b).

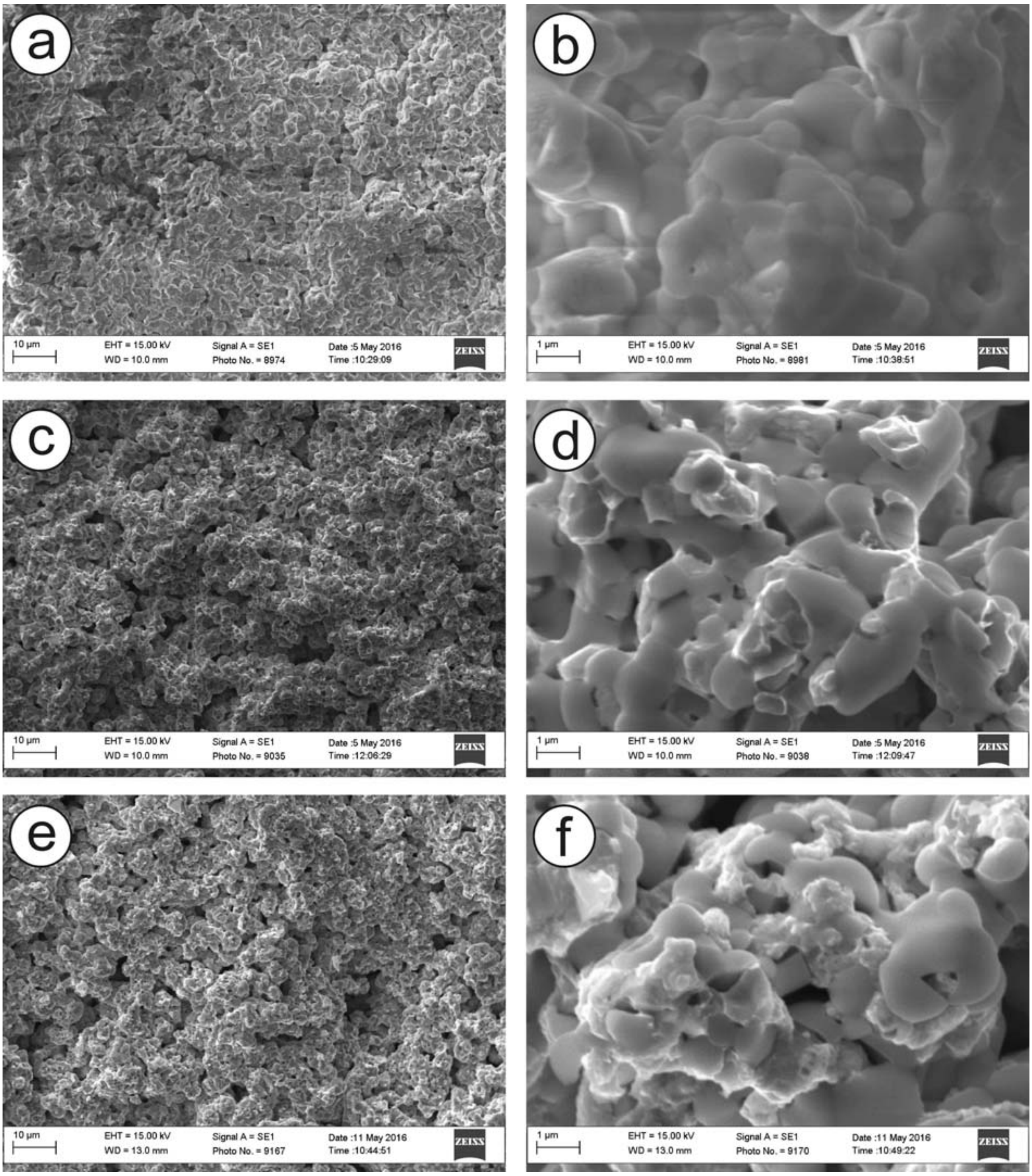

Fig. 2. Observations of the fracture surface morphology of specimens (a, b) A1, (c, d) R1, and (e, f) RO1 at (a, c, e) low and (b, d, f) high magnifications (see Table 1)

In our study, no discernible difference in mechanical behaviour was found for materials tested in mode 2 (see Fig. 1a, b). A small amount of water vapor in Ar–5 vol% H_2 mixture (water vapor pressure below 0.03 MPa) does not affect the reduction of a nickel phase in YSZ–NiO ceramics (see Fig. 3a, b) but causes some changes in the YSZ–Ni cermet structure (see Fig. 3c–f), in particular, growth of nanopores on tiny Ni particles. Resulting strength of the YSZ–Ni cermet decreases by 10–12% as compared to the material reduced in the atmosphere without water vapor. Electrical conductivity of material is of about the same level as for preconditioned series in mode 1 except for A series where it is five times lower, as a result of partial reduction of a nickel phase (mode 2 in Fig. 1c).

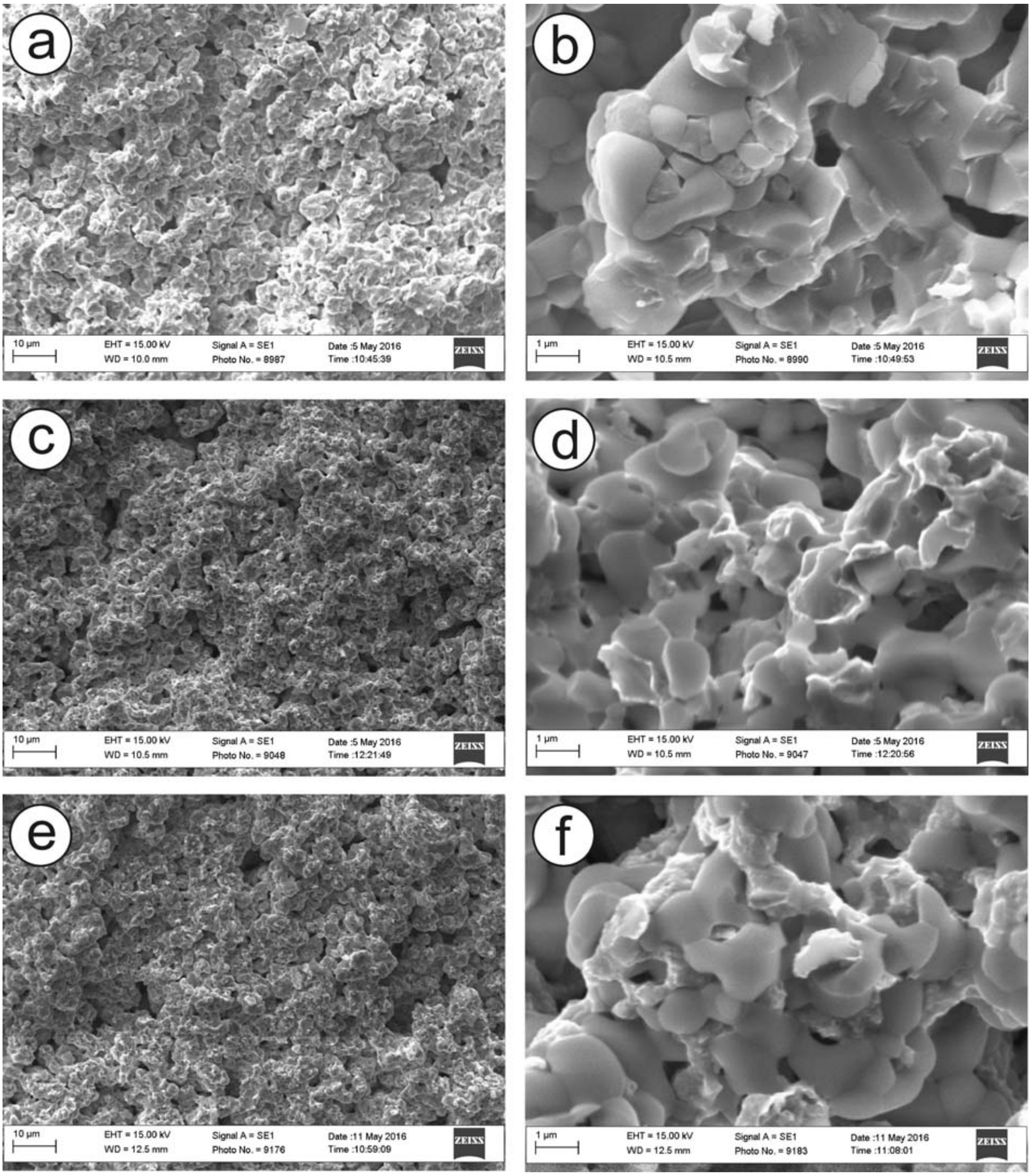

Fig. 3. Observations of the fracture surface morphology of specimens (a, b) A2, (c, d) R2, and (e, f) RO2 at (a, c, e) low and (b, d, f) high magnifications (see Table 1)

For as-received material (A series), high concentration of water vapor in Ar–5 vol% H_2 mixture (water vapor pressure 0.148 MPa) is an obstacle for its reduction. As a result no satisfied value of electrical conductivity for A series was reached (mode 3 in Fig. 1c). A particular increase in strength (mode 3 in Fig. 1a, b) is probably caused by water vapor assisted lowering the residual stresses in YSZ–NiO ceramics [10] because no visible signs of structural degradation are observed (Fig. 4a, b). At the same water vapor concentration, a drastical drop of strength of preconditioned materials was revealed (mode 3 in Fig. 1a, b). Such an atmosphere does not allow the reduction of a nickel phase to occur. In the presence of water vapor of high pressure, re-oxidation of a nickel phase occurs at 600°C and, finally, degradation of YSZ–Ni cermet takes place by debonding smaller particles of nickel phase (Fig. 4c–f), accompanied with slight lowering the conductivity (by 3%). The strength of the one-time reduced material (R series) is lowered by 19% and the cyclically treated one (RO series) – by 27% as compared to the as-received ceramics (mode 3 in Fig. 1a, b).

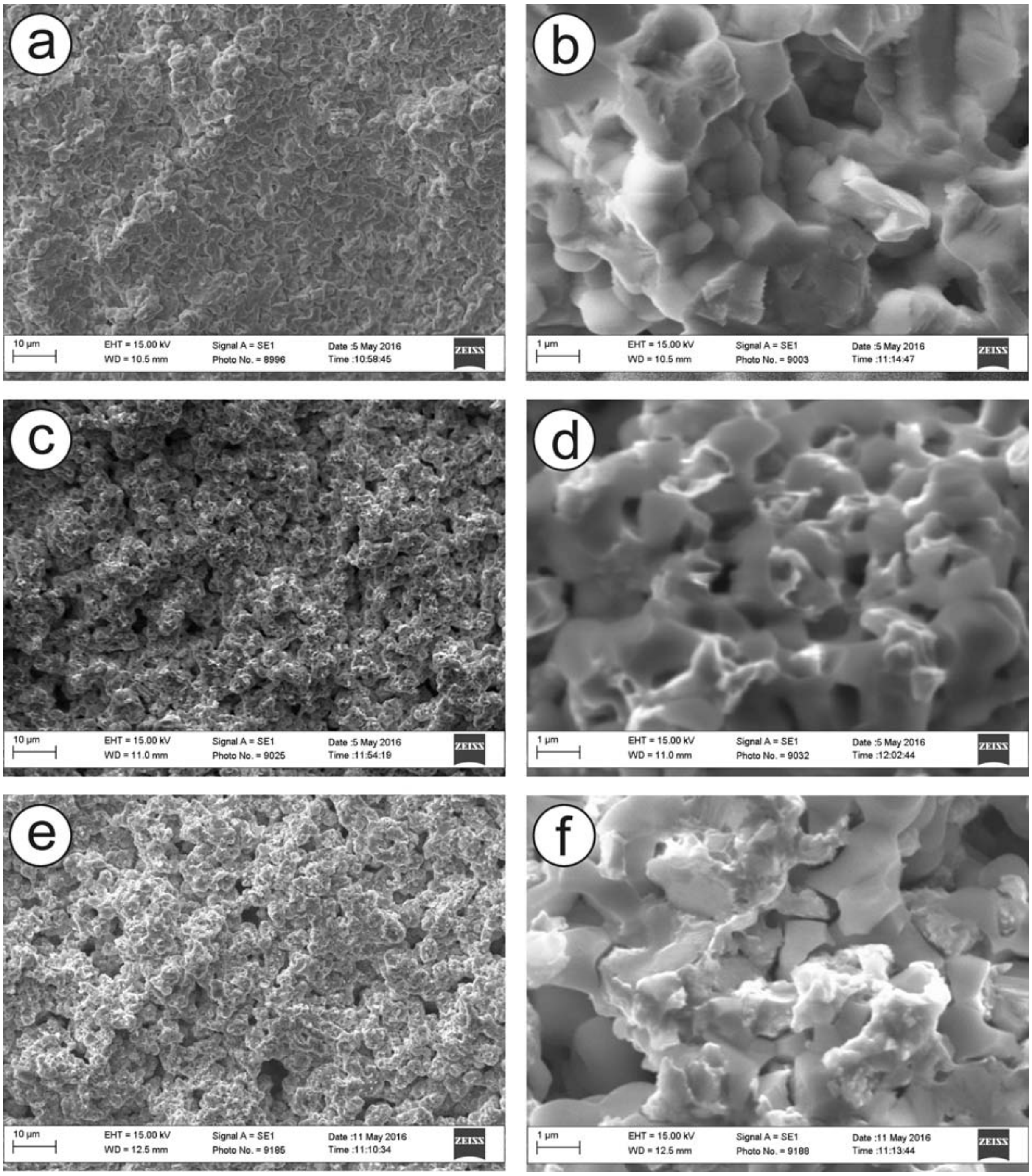

Fig. 4. Observations of the fracture surface morphology of specimens (a, b) A3, (c, d) R3, and (e, f) RO3 at (a, c, e) low and (b, d, f) high magnifications (see Table 1)

Thus, we revealed a positive effect of high amount of water vapor at 600°C on the strength of the as-received ceramics. But in all the cases of preconditioned specimens, deterioration of physical and mechanical properties affected by water vapor of high pressure, was observed. We suppose that such a dual effect of water vapor on durability of a nickel-zirconia anode needs to be an object of forthcoming detailed investigations.

4. Conclusions

Based on the experimental data the dual effect of water vapor on durability of the anodes has been revealed. A small amount of water vapor in Ar–5 vol% H_2 mixture (water vapor pressure below 0.03 MPa) does not affect the reduction of a nickel phase in YSZ–NiO ceramics but causes some changes in the YSZ–Ni cermet structure, in particular, growth of nanopores on tiny Ni particles. Resulting strength of the YSZ–Ni cermet decreases by 10–12% as compared to the material reduced in the atmosphere without water vapor. A higher concentration of water vapor in the mixture (water vapor pressure above 0.03–0.05 MPa) causes a converse change in the reduction kinetics. For as-received material, such an amount of water vapor in the mixture is an obstacle for its reduction. It also causes re-oxidation of a nickel phase in the YSZ–Ni cermet at 600°C. For the material treated by redox cycling, better physical and mechanical properties were revealed after dwelling at 600°C in a water depleted gas mixture. Contrary to this, after dwelling at 600°C in a water enriched gas mixture, the material showed lower resistance against re-oxidation and the lowest strength. We suggest that amount of water vapor in operating hydrogenous media of SOFCs should be limited and water vapor pressure should be below 0.03–0.05 MPa.

5. References

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