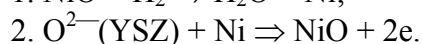
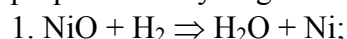


Microstructural and Electrochemical Study of Charge Transport and Reaction Mechanisms in Ni/YSZ Anode

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The microstructure and chemical changes in the Ni-YSZ heterojunctions were studied by scanning, transmission, and high-resolution electron microscopy and X-ray diffraction. It was shown that new nano-size Ni grains are formed at Ni-YSZ interface at the cell operation. The following two stage reaction mechanism was proposed for hydrogen oxidation on the nano-size Ni grains:



This mechanism implies that the SOFC will operate during some time even after switching off the hydrogen flow. We have observed and investigated current-voltage characteristics of SOFC after cutting off the hydrogen pass through anode chamber.

Electrochemical properties of SOFC were investigated as a function of Ni volume content for two different geometry of anode current collector. Good correlations of experimentally measured SOFC characteristics with results of numeric calculations were found.

Introduction

The solid oxide fuel cells (SOFCs) are a new promising technology for electrical power generation because of their high electrical efficiency, low pollution and fuel flexibility. The high operation temperature near 900°C - 1000°C leads to many serious problems such as chemical and mechanical stability of component materials. The operation of the SOFCs at intermediate temperature (600°C-800°C) gives the degradation rate reduction of used materials, but, at the same time, the ohmic loss increase and the electrodes catalytic activities drop down. An improvement of SOFC performance for intermediate temperature operation can be achieved by optimization of anode microstructure and composition. The Ni/YSZ composite is a most reliable and most successful anode system for solid oxide fuel cells. The catalytic and electrical properties of the anode are directly correlated with its microstructure and composition. Despite on numerous experimental data the exact mechanism of a fuel oxidation in the cells is still unclear. In present work we investigated in detail the microstructure and chemical changes in the Ni-YSZ heterojunctions by scanning, transmission, and high-resolution electron microscopy and X-ray diffraction. We proposed an alternative mechanism of fuel (hydrogen) oxidation at three phase boundary (*tpb*) and measured electrochemical properties of model SOFC with two different geometry of anode current collector as a function of Ni volume content.

Experimental

A YSZ disk with a thickness of 0.5mm and a diameter 20mm was used as an oxygen ionic conductor for manufacturing of the solid oxide fuel cell. The NiO-YSZ mixed oxide paste was screen-printed with an area of 2 cm² on the surface of the YSZ disc as the anode and sintered at 1250°-1400°C for 4 hours. In present work we used NiO-YSZ mixed oxides with 25, 35, 45, 55, 65 and 75vol% of NiO. The anodic pastes were prepared by mixing

the obtained powder and polyethylene glycol ($\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OH}$, M.W.=300). The Pt-YSZ paste was screen-printed with an area of 2 cm^2 on to the another surface of the YSZ disk as a cathode, and then sintered at 1200°C for 2 hour. The platinum mesh and wires were attached to the cathode and the anode, to connect with the potensio – galvanostat.

The electrochemical measurements were carried out in a two chamber cell set-up at temperatures between 650°C and 850°C . The fuel gas consisted of a mixture of H_2 and N_2 . In air chamber was supplied by an artificial air containing mixture O_2 and N_2 . The mass flow controllers were employed to maintain well defined gas mixtures and change gases flow rate from $0.1\text{ml}/\text{min}$ up to $100\text{ml}/\text{min}$. The electrochemical impedance measurements were carried out with an Agilent 4294A precision impedance analyzer. The current-voltage characteristics of SOFCs were measured by home made potensio – galvanostat LSDC-01 in a four-point method.

The microstructure and chemical element distribution through the cross-section of the mixed oxide electrode were examined with a scanning electron microscope ZEISS-SUPRA-50 VP.

Results and Discussion

For development of the efficient SOFC operating at intermediate temperature the ohmic losses in composite anode should be diminished. It results in the task on optimization both electrical conductivity and adequate porosity for gas transport. The cell performance is governed by the electronic resistivity of the Ni particles, overpotentials associated with charge-transfer at the electronic (Ni)-ionic (YSZ) conductors and gas phase boundaries and the ionic conductivity of solid electrolyte. It is generally recognized that the slow interfacial (charge-transfer) reaction rate at the *tpb* is often responsible for the SOFC electrode restrictions [1-3]. Thus it is necessary to fabricate the mixed oxide anode with three dimensional network pathways for oxygen ions migration from the YSZ disc to the *tpb* and simultaneously retaining a three dimensional network pathways for the electrons migration from *tpb* on the surface inside anodic pores to a current collector.

Optimization of the $\text{NiO}_x\text{-YSZ}_{1-x}$ anode microstructure

In the work, we examined the sintering temperature effect on the NiO-YSZ cermet anode microstructure. The microstructure and chemical element investigations were performed with a scanning electron microscope ZEISS-SUPRA-50 VP on the cross section of the SOFC disc. Figure 1 demonstrates the cross section images of the NiO-YSZ mixed oxide anodes sintered for 4 ours at 1250°C , 1300°C , 1350°C and 1400°C . It is seen that increase of the sintering temperature results in the decrease of the average pore sizes in the ceramic anode and formation of the dense boundaries between NiO-NiO and YSZ-YSZ grains which create two interpenetrate three-dimensional networks for electronic and oxygen ionic migration. Moreover the average size of NiO and YSZ grains remain practically the same and only slightly increase with the sintering temperature. The measurements of the single cell performance vs. NiO-YSZ anode sintering temperature has shown that the power density sharply increases in the range $1250\text{-}1350^\circ\text{C}$ and becomes practically independent above 1350°C (Fig.2).

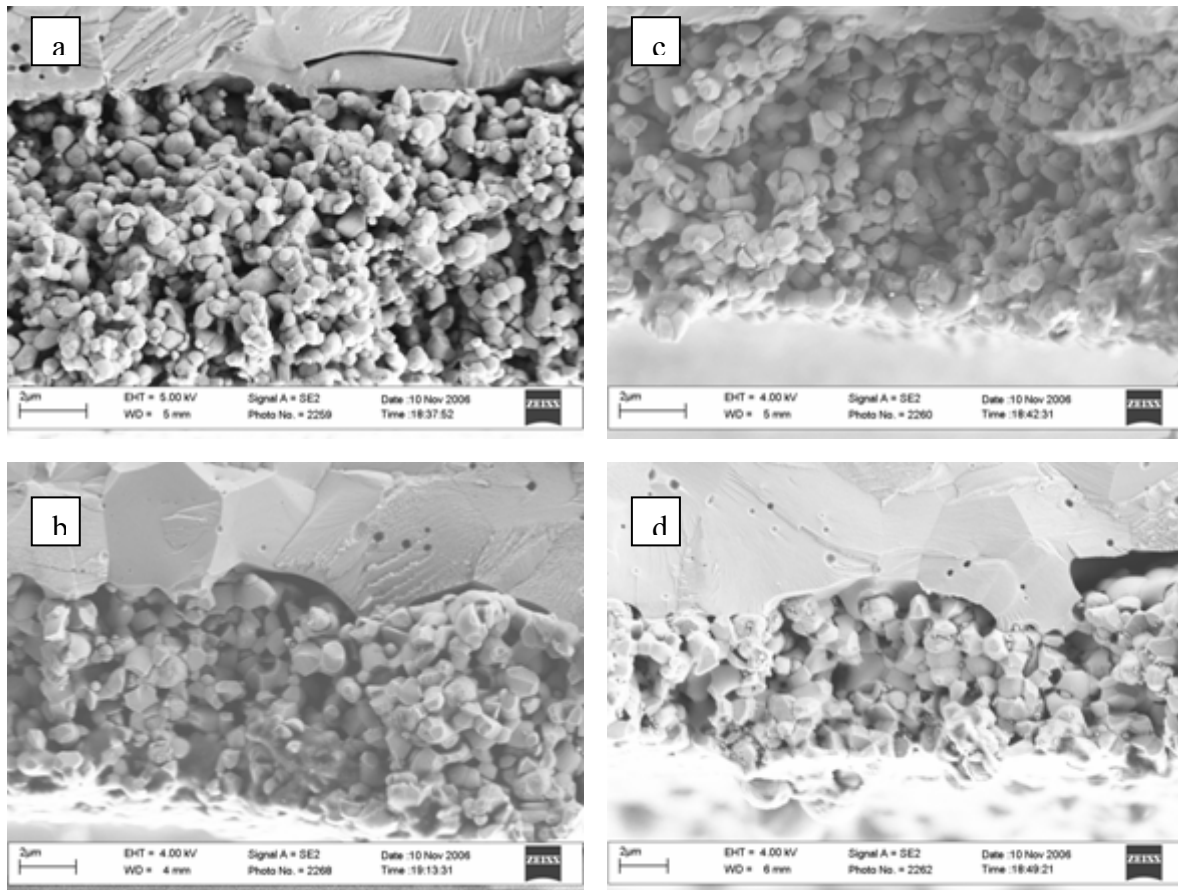


Fig.1. The cross-section view of the mixed oxide anode sintered at 1250°C (a), 1300°C (b), 1350°C (c) and 1400°C (d).

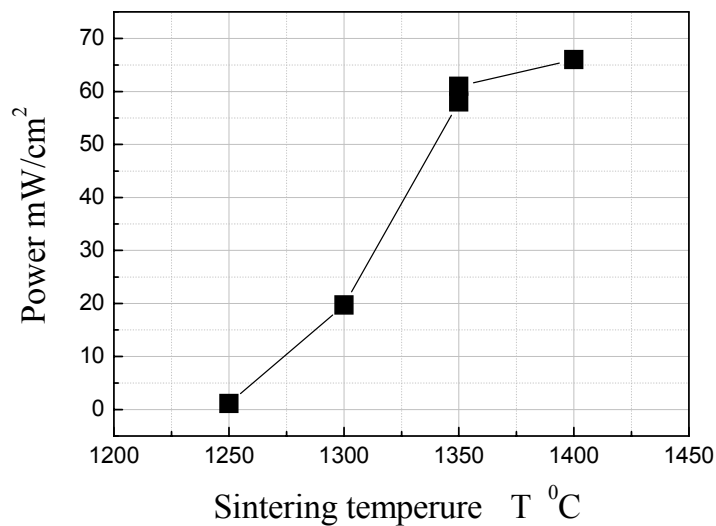


Fig.2. SOFC power as function of sintering temperature of Ni-YSZ anode.

In accordance with this result we have further sintered the NiO-YSZ anodes at 1380°C. The detail microstructural investigations of the Ni/YSZ interface have shown that new Ni nano-grains are formed near Ni/YSZ interface region after the cell operation. To describe this phenomenon we proposed that new small NiO grains originate from the initial Ni one

at the current flux through the cell. When the value of the current through the cell decreases than it takes place reduction of these new NiO grain with formation of a new small Ni grains. It is obvious that new Ni grains would locate in the regions bordered the Ni/YSZ interfaces and that they should be arranged in direct contact with YSZ grains.

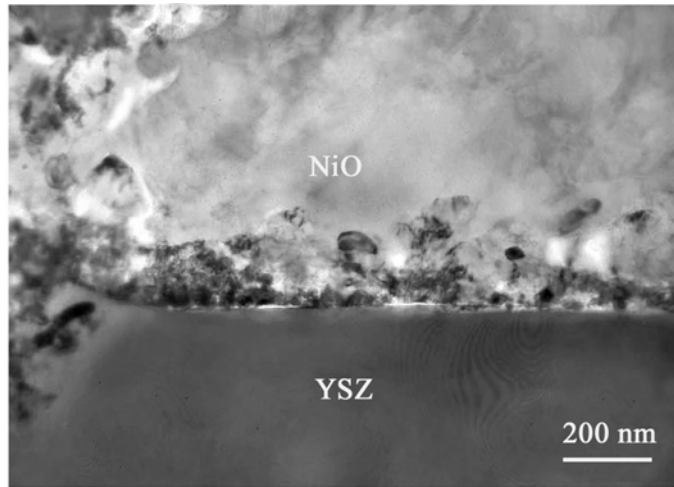


Fig.3. TEM image of an interfacial boundary between YSZ and NiO grains after cell operation.

In our previous observation of the NiO/YSZ interface structure evolution of electrochemical cells [4,5] we found that new small NiO grains are formed around the untransformed central part of the NiO particles after cell operation (Fig.3).

The structure evolution analysis on Ni-YSZ heterojunctions allowed us to propose the

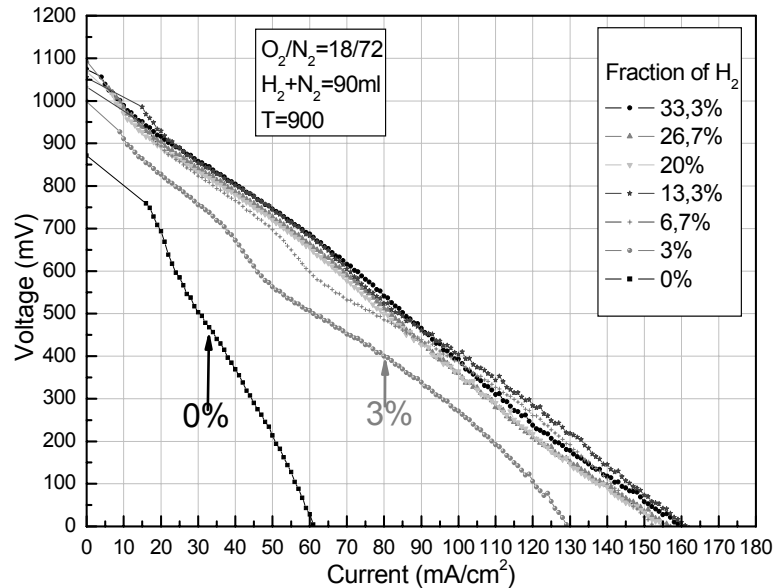


Fig.4. The voltage-current SOFC data as functions of the H₂ content in fuel gas.

following two stage reaction mechanism for hydrogen oxidation during the cell operation:

1. $\text{NiO} + \text{H}_2 \Rightarrow \text{H}_2\text{O} + \text{Ni}$;
2. $\text{O}^{2-}(\text{YSZ}) + \text{Ni} \Rightarrow \text{NiO} + 2\text{e}^-$.

This mechanism implies that the SOFC will operate for some time even after switching off the hydrogen flow. Our experiments completely confirmed this assumption.

The typical $I-U$ characteristic of SOFC operating at different volume content of H_2 in fuel gas represented in Fig.4. It is seen that SOFC can operate even after cutting off the hydrogen pass through anode chamber. This result is a direct evidence of the efficiency of two stage reaction mechanism of hydrogen oxidation on the nano-size Ni grains produced during the cell operation.

Additionally we should mention that artificial formation of a nano-size Ni grain boundary region between Ni and YSZ grains should leads to drastic decrease of the overpotentials associated with charge-transfer at the electronic (Ni)-ionic (YSZ) conductors and gas phase boundaries.

Optimization of the NiO_x-YSZ_{1-x} anode microstructure for different geometry of anode current collectors.

It is well known that SOFC properties depend on many individual phenomena and that the geometry of current collector is one of the most important parameter which effect drastically on the SOFC efficiency. Since the Ni-YSZ anode is composite ionic – electronic conductor then the volume content of electronic (Ni) and ionic (YSZ) phases should be optimized depending on the current collector geometry.

In present work electrochemical properties of SOFC were investigated for two different geometry of anode current collector as a function of Ni volume content.

“Plane” geometry of current collector

The typical example of “plane” geometry of anode current collector is pores metal supported SOFC. In such cell there is no component of current flux in the anode plane and all optimizations of anode resistance in the geometry are associated with optimization of the ambipolar conductivity value.

It is obvious that for the reduction of the ohmic loss it is necessary to design the anode with high electrical conductivity and adequate porosity for gas transport. Moreover the optimized composite anode should contain a three dimensional network of pathways for the oxygen ions migration from the YSZ disk to *tpb* and interpenetrated three dimensional network of pathways for the electrons migration from the current collector to *tpb* on the surface of the inside anode pores.

The SOFC efficiency investigations with different NiO-YSZ anode compositions have

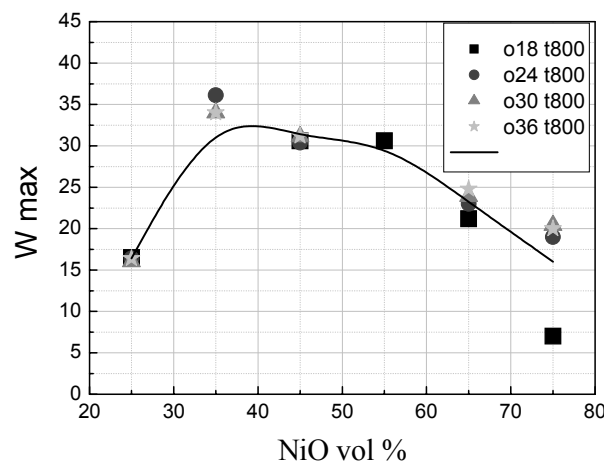


Fig.5. SOFC power as a function of Ni volume content in the composite anode for SOFC with “plane” geometry of current collector.

shown a strong dependence of cell power vs. the Ni volume content (Fig.5).

It is seen from the Fig.5 that the efficiency of SOFCs with “plane” geometry of current collector increases with increasing of the NiO content from 20 to 35 vol% and smooth decrease above 35 vol%. The best performance was observed for cells with NiO concentration around 35vol%.

To clarify this strong dependence of the SOFC efficiency versus the NiO-YSZ anode composition we have analyzed the cell electrical properties with different composite anodes. The electrical properties of mixed ionic – electronic conductors depend critically on the ambipolar transport properties of the composites [6]. In accordance with the prediction of the effective medium percolation theory in a mixed oxide $\text{NiO}_x\text{-YSZ}_{1-x}$

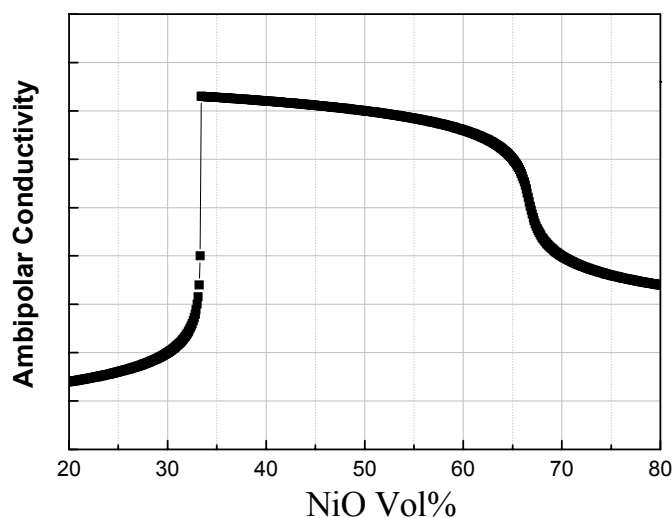


Fig. 6. The ambipolar conductivity dependence versus the volume fraction of NiO in the composite NiO-YSZ anode.

electrode a sharp transition in the effective conductivity should be observed (Fig.6) [6]. The percolation threshold occurs at $x = 1/3$ for effective electronic and ambipolar conductivity and at $x = 2/3$ for effective ionic and ambipolar conductivities. This means that the NiO phase becomes continuous when its volume fraction is greater than $1/3$ and the YSZ phase becomes disconnected when the volume fraction of NiO phase is greater than $2/3$. The two percolation thresholds reveal a composition range from $1/3$ to $2/3$, in which the ambipolar conductivity is much higher than in other regions.

In accordance with these results, a sharp transition in the efficiency of SOFC with “plane” geometry of current collector was observed when the volume content of NiO in the NiO-YSZ anode is slightly greater than $1/3$. Therefore the highest efficiency of SOFC with “plane” current collector geometry is reached when the ambipolar conductivity of the composite electro-catalytic electrode has a maximum value.

The “point” geometry of current collector.

The typical examples of the “point” geometry of anode current collector are anode or cathode supported SOFC. A current flux along the anode plane are realized in the cells which results in necessity of a high electronic conductivity along the anode.

The investigations of the SOFC efficiency with the “point” current collector geometry heve revealed a strong dependence of the cell power versus the NiO volume content of the NiO-YSZ anode composition (Fig.7).

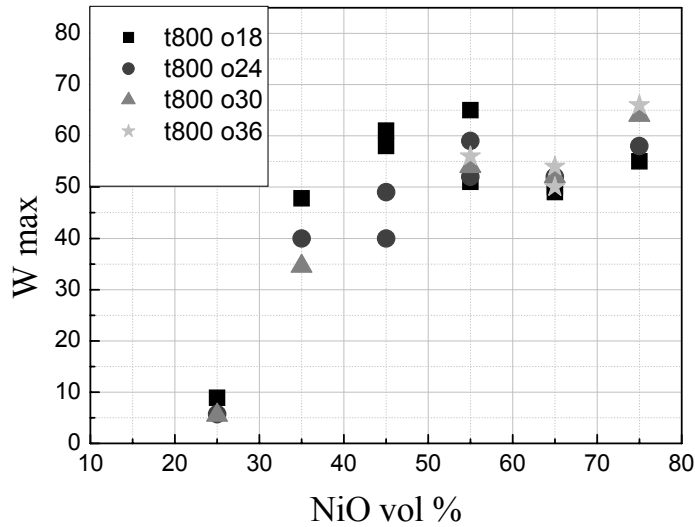


Fig.7. The maxima power as a function of Ni volume content in the composite anode of SOFC with “point” current collector geometry.

It is seen from the Fig.7 that with this current collector geometry the SOFC efficiency rapidly rise in the range from 25 to 35 NiO vol% and then gradually increase at the concentrations above 35 NiO vol%.

Our numerical calculations of the electronic conductivity value versus the $\text{NiO}_x\text{-YSZ}_{1-x}$ compositions represented on Fig.8 and is in well accordance with the prediction of the effective medium percolation theory [6].

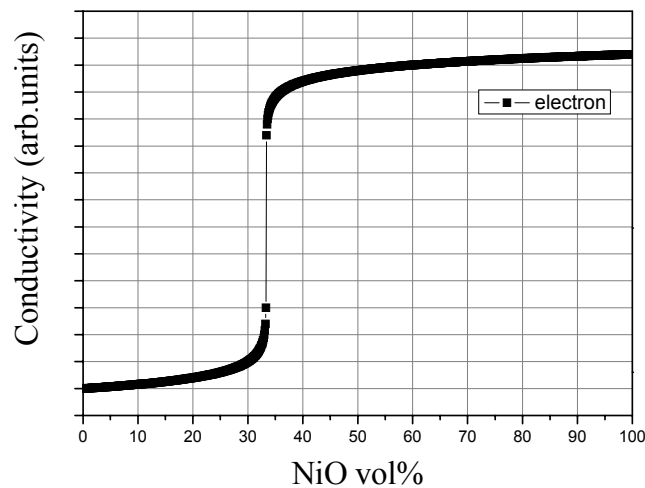


Fig.8. The dependence of the electronic conductivity value of the composite anode vs. the volume fraction of NiO.

The experimental (Fig.7) and simulated (Fig.8) data indicate that the SOFC performance with the “point” current collector geometry depends mainly on the anode electronic conductivity. The best performance in the case was observed for cells with of NiO content near the second percolation threshold (2/3).

Conclusion

The nano-size Ni particles formation was observed between Ni and YSZ grains in Ni-YSZ composite anode. The two stage reaction mechanism was proposed for hydrogen oxidation on the nano-size Ni grains produced during the cell operation. Our experiments have shown that this two stage mechanism is responsible for SOFC operation during some time after switching off the hydrogen flow.

A sharp transition in the efficiency of SOFC with “plane” current collector geometry was found at the NiO volume content around the first percolation threshold of 1/3. The highest efficiency of SOFC in the geometry can be reached when the ambipolar conductivity of the composite electro-catalytic electrode has a maximum value.

The SOFC performance with the “point” current collector geometry depends mainly on the electronic conductivity of the anode. The best performance in the case was observed for cells with of NiO content near the second percolation threshold (2/3).

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