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Anode Materials for Solid Oxide Fuel Cells

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Abstract

The ceramic-metal composites (cermets) containing yttria-stabilized zirconia, YSZ, and Ni particles are commonly used as anode materials in solid oxide fuel cells. The long-term performance of fuel cells is strictly related to both the structural and electrical properties of anode materials. The chemical composition and preparation method are key to achieving high mixed electrical conductivity and high activity of electrochemical reactions and hydrocarbon fuel reforming. The materials containing 8 mol.% yttria-stabilized zirconia and Ni were prepared by co-precipitation method. The structure of the materials was characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and porosity studies. The coefficient of thermal expansion (CTE) was determined via a dilatometric method. Electrochemical impedance spectroscopy (EIS) was used to determine electrical conductivity.

Keywords: Anode, SOFC, Cermet materials, Ni-YSZ

MATERIAŁY ANODOWE DLA PALIWOWYCH OGNIW STAŁOTLENKOWYCH

Kompozyty ceramiczno-metaliczne (cermety), zawierające dwutlenek cyrkonu stabilizowany Y_2O_3 (YSZ) i cząstki Ni są powszechnie wykorzystywane jako materiał anodowy w stałotlenkowych ogniwach paliwowych. Długoterminowe osiągi ogniw paliwowych są ściśle związane zarówno ze strukturą, jak i z elektrycznymi właściwościami materiałów anodowych. Skład chemiczny i metoda wytwarzania stanowią klucz do osiągnięcia wysokiej, mieszanej przewodności elektrycznej i wysokiej aktywności reakcji elektrochemicznych oraz reformingu paliwa węglowodorowego. Materiały zawierające Ni i dwutlenek cyrkonu stabilizowany 8 % mol. Y_2O_3 wytworzono metodą współstrącania. Budowę materiałów scharakteryzowano za pomocą dyfraktometrii rentgenowskiej (XRD), elektronowej mikroskopii skaningowej (SEM) i badań porowatości. Współczynnik rozszerzalności cieplnej (CTE) określono metodą dylatometryczną. Elektrochemiczną spektroskopię impedancyjną (EIS) wykorzystano do określenia przewodności elektrycznej.

Słowa kluczowe: anoda, SOFC, cermetal, Ni-YSZ

1. Introduction

Nickel-based cermet materials are commonly used as an anode in solid oxide fuel cells [1]. They are used either in two chamber [1] or single-chamber cell involving oxygen [2] or hydrogen [3] ion conducting solid electrolytes. The metallic component acts as electronic conductor. Moreover, it is an excellent catalyst for breaking hydrogen bonds and shows low reactivity with other cell components and can be produced at a fairly low cost. However, significant problems arise using hydrocarbons as cell fuels. For example, direct oxidation of the methane, despite favourable thermodynamics, is a slow process due to carbon deposition. In order to avoid carbon deposition, a ratio H_2O:CH_4 greater than three is required [4]. Using gas mixture containing water and methane, the internal reforming of hydrocarbon on nickel electrode can be achieved [5]. High performance anode needs sufficient concentration of three phase boundaries, TPB, where fuel molecules, oxygen ions keep contact with along electric conduction paths.

This can be realized by using materials containing enough open porosity. So, using only nickel phase as anode materials, the TPB are located at the interface electrode/electrolyte due to the fact that oxygen ions originate from the electrolyte only. Moreover, there are several problems such as thermal expansion coefficient, TEC, of nickel being considerable higher than that of the electrolyte such as YSZ, thus nickel easily sinters at higher temperatures, which results in a decrease in the anode porosity. These problems are solved by forming a matrix of YSZ around nickel particles. YSZ component provides a substantial enlargement of the electrochemical reaction zone, enhances the electrode stability and adherence to the electrolyte, especially to adjust thermal expansion coefficient [6, 7]. Since the anode material should provide percolation paths for electrons, oxygen ions and gases, the electrochemical performance is closely related to the electrode microstructure [8-10].

The aim of this work was the determination of the effect of the cermet preparation method on both structural and electrical properties of the cermet.

2. Experimental procedure

2.1. Preparation of materials

A co-precipitation method was used to prepare yttria-zirconia solid solutions with the 8 % mol of yttria. Aqueous solutions of zirconium nitrate with an appropriate amount of yttrium nitrate were introduced into the ammonia solution. Nickel nitrate was introduced to one part of the yttria-zirconia materials as a precursor of nickel. Yttria-zirconia and yttria-zirconia with 50 wt% of nickel were then added to this part of preparation. The resulting gels were washed with water, dried, and calcined at the temperature of 700°C for 1 hour. The ground powders were pressed under 200 kPa and then sintered in air at 1300°C for 3 hours. All pellets were reduced in 5 % H_2/Ar at 800°C for 6 hours.

2.2. Microstructure and XRD

The phase composition of all sintered samples was characterized by X-ray diffraction analysis. Measurements were performed on X'Pert MPD Philips diffractometer within the range of diffraction angles 2θ from 10° to 80° with the Cu-K filtered radiation. Crystallographic and phase analysis was carried out by means of an implemented program of line profile analysis, LPA. Open porosity was measured by the water saturation method. Scanning electron microscopy (SEM) pictures of powders were recorded with FEI NOVA NanoSEM 200 supported by BSED detector.

2.3. Dilatometric studies

Dilatometric studies were carried out in the prototypical dilatometer with the measuring instrument and „size changing" transducer of Jota Company. The process was carried out in air in the temperature range of 20-800°C. The coefficients of thermal expansion were calculated for all samples.

2.4. Electrochemical impedance spectroscopy

The electrical properties of yttria-zirconia-based. solutions were investigated by ac electrochemical impedance spectroscopy in the temperature range of 20-800°C and at the frequencies, *f,* from 0.1 Hz to 10^6 Hz. The measurements were taken on Solartron SI1260 Impedance/gain-phase analyzer with the SI 1287 Electrochemical interface.

3. Results and discussion

Table 1 summarizes chemical composition, porosity and the coefficient of thermal expansion, CTE, of the studied materials.

Table 1. Main characteristics of the studied materials.

Sample	[wt%] Ni	Porosity [%]	CTE [$10^{-5}K^{-1}$]
30 [N]	30	49.2	1.13
48 [N]	48	49.2	1.32
50 [N]	50	50.8	1.51

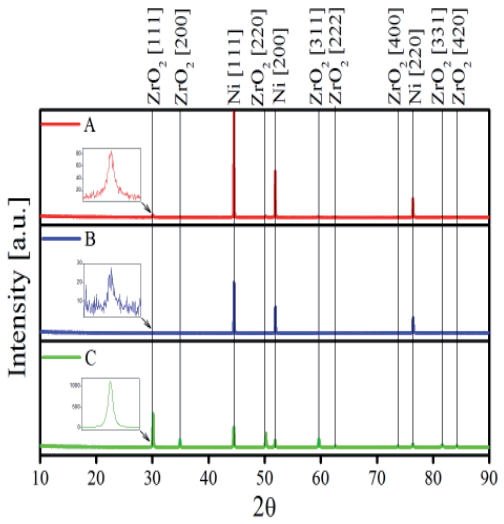


Fig. 1. XRD patterns of the studied materials.

Fig. 1 shows the XRD patterns of studied samples marked as 30 N, 48 N and 50 N (according to Table 1). Diffraction patterns are typical for highly crystalline materials. It was found that the samples are composed from the Ni and YSZ phases. No additional phases were found.

SEM micrographs of the sintered samples are shown in Fig. 2. All samples are composed of large grains (*ca*. 1 - 3 μm) of nickel forming continuous phase. In samples containing *ca*. 50 wt% Ni, the percolation threshold was exceeded. On the other hand, nanometric grains of YSZ are visible in Fig. 2. The sample # 50 N is much more uniform that that # 30 N & 48 N.

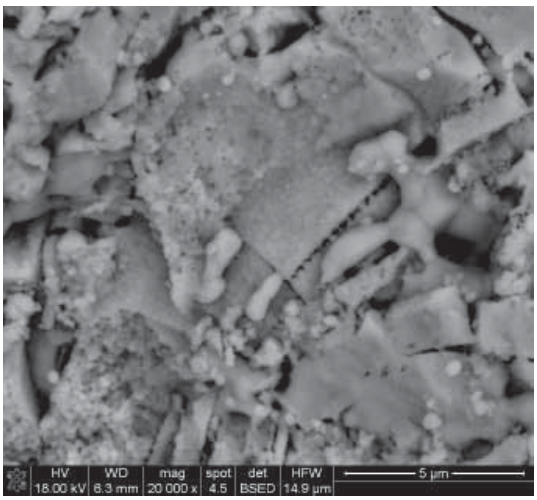
Fig. 3 illustrates dilatometric results of the sample 30 N, as an example. The experimental points can be approximated by two straight-lines. The first line, corresponding to low-temperature range (between room temperature and *ca*. 500 K) was used to determine coefficient of thermal expansion, CTE, characteristic for the cermet material. At higher temperatures the slope is changed due to partial oxidation of the metallic phase. As visible from the Table 1, the value of CTE depends on both: chemical composition and method of cermet preparation. The determined CTE's are between the values of YSZ ($1.05 \cdot 10^{-5} \cdot K^{-1}$) [1] and Ni ($1.7 \cdot 10^{-5} \cdot K^{-1}$) [11].

The impedance data were analyzed in terms of equivalent circuit [12]. Fig. 4 illustrates the Bode plot of absolute value of impedance |*Z*| of the sample 50 N at 673 K. This plot is similar to that presented in inset of the Fig. 4. corresponding to the equivalent circuit composed from *L*-*R*-*C* elements connected in series. *L* is the inductance which could be due to Ni cermet component and electrode wires, *R* is the overall ohmic resistance and *C* (or constant phase element, *CPE*) is the capacitance of the sample.

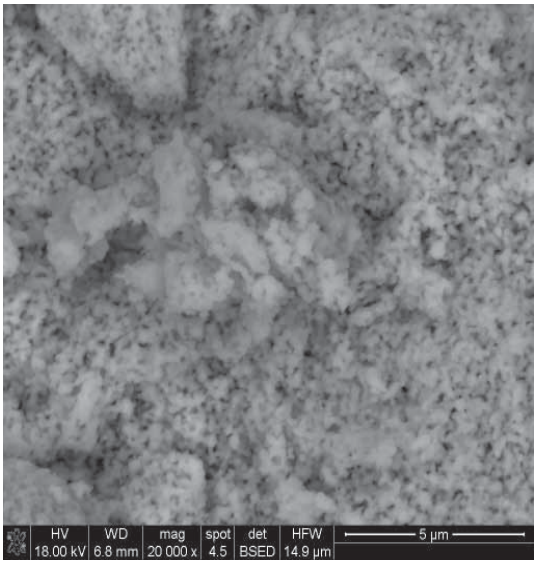
Table 2. The L and R values calculated for the studied materials.

Sample	*L* [H]	*R* [W]
30 [N]	$2.5925 \cdot 10^{-6} \pm 2.38\%$	2.304±1.367%
48[N]	$2.3508 \cdot 10^{-6} \pm 2.45\%$	2.315±1.515%
50[N] *	$2.5290 \cdot 10^{-6} \pm 3.12\%$	2.468±2.460%
50[N] **	$2.6413 \cdot 10^{-6} \pm 0.976\%$	2.088±0.5124%

* - *dielectric interface,* ** - *electrochemical interface*



a)



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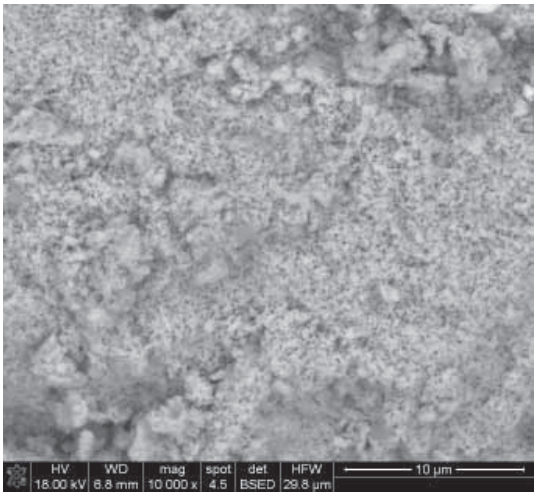

c)

Fig. 2. SEM micrographs of the sintered samples: a) 30 N, b) 48 N and c) 50 N.

The impedance data of the sample 50 N at 673 K within frequencies between 1kHz - 1MHz are presented on complex admittance plane *Y"* versus *Y'* in Fig. 5. Well developed semicircle with the center on the *Y'* axis is visible. The position of the centre on the Y' axis indicates that a Debye capacitor can

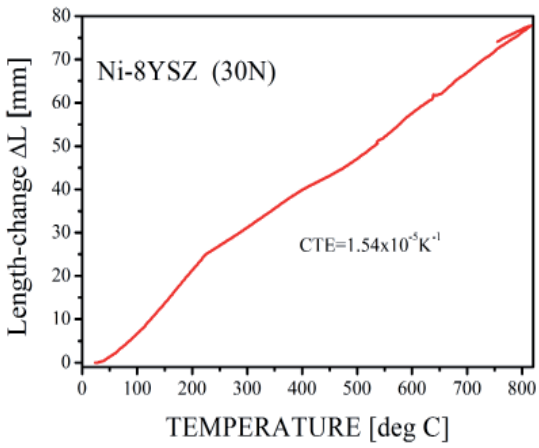

Fig. 3. Dilatometric results of the sample 30 N.

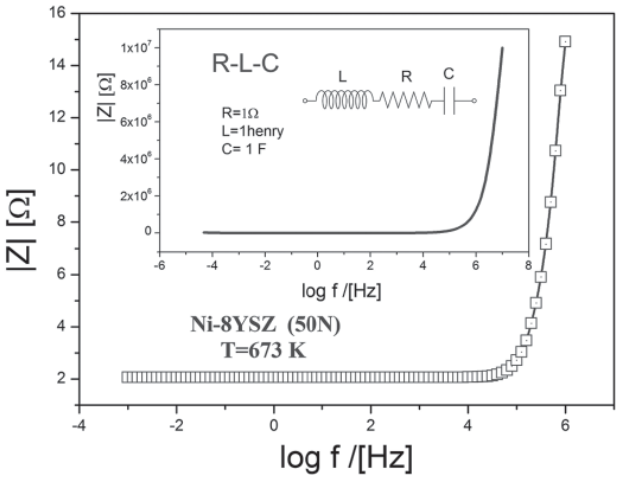

Fig. 4. Bode plot of the absolute value of impedance |Z| of the 50 N at 673 K and the equivalent circuit (inset).

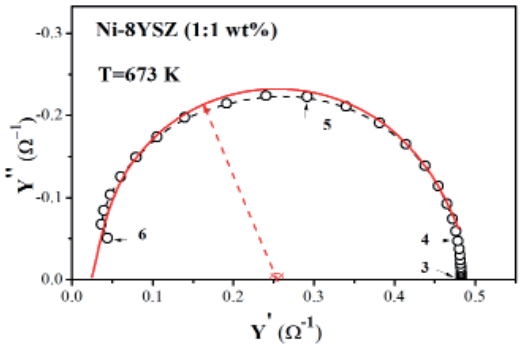

Fig. 5. Admittance spectrum of the 50 N at 673 K. Numbers denote logarithm of frequencies.

be used in the equivalent circuit instead of the *CPE* element. Similar results were obtained for other samples. The values of *L* and *R* obtained from fitting the impedance data with the equivalent circuit illustrated in Fig. 4 are shown in Table 2. The capacitance values, *C*, were of the order of several µF but they exhibit high scatter.

Fig. 6. illustrates the dependence of electrical resistivity on temperature for all studied samples. The observed increase of resistivity with temperature indicates metallic behaviour of the studied materials due to the presence of nickel particles in cermet materials (Figs. 1 and 2).

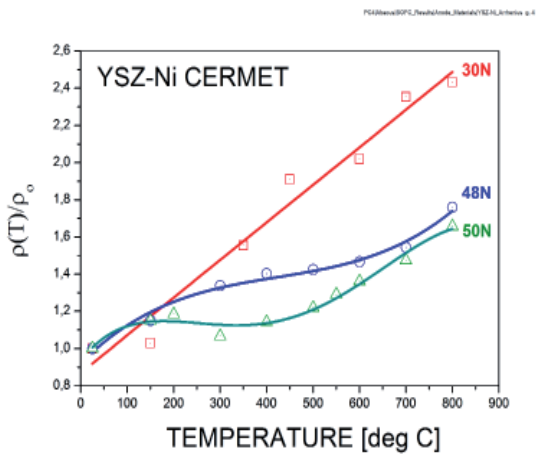

Fig. 6. Temperature dependence of the electrical resistivity, ρ_o – resistivity at room temperature.

The temperature dependence of electrical resistivity of metals is given by the theoretical dependence known as Bloch-Gruneissen formula [13]:

$$\rho(T) = \rho_0 + A\left(\frac{T}{\Theta_R}\right)^n \cdot \int_0^{\frac{\Theta_R}{T}} \frac{x^n}{\left(e^x - 1\right)\cdot\left(1 - e^{-x}\right)} dx \qquad (1)$$

where $\rho(T)$ – electrical resistivity at T, ρ_0 – residual resistivity, A – constant, Θ_R - Debye temperature, n – parameter assuming the following values depending on the mechanism of charge scattering:

n = 5 implies that the resistance is due to scattering of electrons by phonons (as it is for simple metals);

n = 3 implies that the resistance is due to s-d electron scattering (as is the case for transition metals);

n = 2 implies that the resistance is due to electron-electron interaction.

The dependence (1) is usually approximated by the power series like following:

$$\rho(T) = \rho_0 \cdot [1 + \alpha\cdot(T - T_0) + \beta\cdot(T - T_0)^2 + \gamma\cdot(T - T_0)^3 + \delta\cdot(T - T_0)^4] \qquad (2)$$

The parameters: ρ_0, α, β, γ and δ of the studied cermet materials, as well as the literature data of nickel bare, are listed in Table 3.

Table 3. The ρ_o, α, β, γ and δ parameters of the studied cermet materials and nickel bare.

Sample	ρ_o, [Ω·cm]	$\alpha\cdot10$ K^{-1}	$\beta\cdot10^6$ K^{-2}	$\gamma\cdot10^9$ K^{-3}	$\delta\cdot10^{12}$ K^{-4}
30N	1.178 ±0.004	2.02 ±0.15	0	0	0
48N	1.516 ±0.006	2.46 ±0.47	4.8 ±1.4	3.8 ±1.1	0
50N	1.594 ±0.009	3.00 ±0.98	15 ±5	27 ±10	15 ±6
[14]	$6.84\cdot10^{-6}$	6.9	0	0	0
[15]	–	5.866	0	0	0
[13]	–	5.45	6.65	0	26.95

The substantial differences between the data corresponding to the cermet materials and nickel bare are observed. These may result from the differences in microstructures, as well as from the effect of solid electrolyte component of cermet.

4. Conclusions

Cermet materials containing ZrO_2 + 8 mol.% Y_2O_3 (8YSZ) and Ni composites were prepared using co- precipitation method. XRD analysis revealed that the composites were composed from well crystallized phases of 8YSZ and Ni. The porosity of material was ca 50 %, the coefficient of thermal expansion (CTE) varied between 1.1 10^{-5} K^{-1} and 1.5 10^{-5} K^{-1}.

Electrochemical impedance spectroscopy was used to determine electrical properties of the studied materials. The equivalent circuit used for fitting the impedance spectra consists of R-L-C elements connected in series. The temperature dependence of electrical resistivity remains in qualitative agreement with metallic properties. However, the quantitative comparison of experimental results with the literature data for Ni-bulk specimens showed considerable differences.

Acknowledgement

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