

PREPARATION OF NiO/YSZ POWDERS USING A PECHINI-TYPE METHOD

PRIPRAVA NiO/YSZ PRAHOV S PRILAGOJENO PECHINI METODO

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Nickel-oxide-yttria-stabilized zirconia (NiO-YSZ) powder mixtures were prepared using a Pechini-type sol-gel route. Metal chlorides/nitrates and citric or ascorbic acid were used to prepare the metal-carboxylic acid complexes. Their subsequent polyesterification with ethylene glycol at moderate temperatures yielded a homogeneous polymer resin. During the thermal treatment of such a 3D resin up to 900 °C metal oxides were formed. In order to optimize the process the influence of the anionic part of the metal precursor and the molar ratio of the complexing agent, e.g., carboxylic acid, and the ethylene glycol was studied.

The properties of the as-synthesized powders were determined using X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), and BET surface area analysis. The sintering behaviour of the sample powder mixtures was studied with a heating microscope. The selection of metal chlorides or nitrates for precursors as well as the variations in the molar ratios of all the starting components affected the cross-linking within the polymer and also the characteristics of the NiO/YSZ products. Their properties determine whether they are suitable as anodic materials for solid-oxide fuel cells.

Keywords: NiO/YSZ powders, Pechini-type method

Anodni material, sestavljen iz nikljevega oksida in cirkonijevega dioksida, stabiliziranega z itrijem (NiO/YSZ), smo pripravili z modificirano metodo Pechini. Z raztapljanjem kovinskih kloridov/nitratov in citronske oziroma askorbinske kisline nastane stabilen kompleks med kovinskimi ioni in karboksilno kislino. Ob dodatku etilen glikola v raztopino prekurzorjev poteče polimerizacija karboksilne kisline in stabilnih kompleksov že pri nizkih temperaturah, pri čemer nastane homogena polimerna smola. Med toplotno obdelavo takšne 3D-smole do 900 °C nastanejo kovinski oksidi. Zaradi optimizacije procesa smo spremljali vpliv anionskega dela kovinskega prekurzorja in množinskega razmerja med karboksilno kislino in etilen glikolom na fizikalne lastnosti končnih produktov.

Tako pripravljene keramične prahove smo analizirali z rentgensko praškovo difrakcijo (XRD), vrstičnim elektronskim mikroskopom (SEM) in z analizo specifične površine prahov (BET). Sintranje dobljenih prahov smo spremljali s segrevalnim mikroskopom. Kovinski kloridi oziroma nitrate kot prekurzorji ter molsko razmerje začetnih komponent je imelo velik vpliv na nastanek polimerne smole in na fizikalne karakteristike produktov NiO-YSZ. Njihove končne lastnosti odločajo o primernosti uporabe za anodne materiale pri gorivnih celicah s trdnim elektrolitom.

Ključne besede: prahovi NiO-YSZ, metoda Pechini

1 INTRODUCTION

Nickel-oxide-yttria-stabilized zirconia (NiO-YSZ) composites are the most commonly used anode materials for solid oxide fuel cells (SOFCs) due to the high catalytic activity of nickel for fuel oxidation. In recent years a lot of research has been done in this field. However, the problems connected with the material preparation techniques have not been completely solved yet. Currently, the most frequently used method for manufacturing the anode is a solid-state technique involving mechanical mixing of the NiO and YSZ powders¹. The method is simple to use; however, the disadvantages of this method are large differences in the powder density and the separation of phases that are present. The final consequence of this is a non-uniform distribution of the nickel particles in the YSZ matrix and inappropriate microstructure of the anode.

Recent studies on the preparation of small particle size NiO-YSZ powders have been focused on other preparation techniques, such as gel-precipitation², spray

pyrolysis³ and solution combustion synthesis⁴. Currently, powders with a good sinterability have been obtained using mixtures with carboxylate, urea and/or glycine^{4,5}. The powders are prepared from the precursor solution, which is subsequently concentrated under vacuum. The obtained products have uniformly distributed nickel particles in the ceramic matrix. The disadvantage of this method is the thermal explosion with no control of the synthesis temperature.

In order to overcome the mentioned weak points, in the present work a modified Pechini method was used to prepare the NiO-YSZ composites. Although only little is known about the chemistry involved in the Pechini route, the basic chemistry of the process is the dehydration reaction of a α -carboxylic acid and an alcohol, i.e., esterification⁸. The resulting polymeric resin comprises randomly branched polymer molecules throughout which the cations that were present in the starting aqueous solution are uniformly distributed. The resin is then thermally treated at elevated temperatures in order to obtain a mixture of metal oxides.

In this paper the influence of various parameters on product characteristics such as thermal properties, sintering behaviour, specific surface area and particle size distribution were determined. In the experiments the following reaction conditions were changed:

- molar ratios between the citric acid and the ethylene glycol,
- metal precursors: chlorides or nitrates were used as starting compounds
- complexing agents: citric or ascorbic acid.

2 EXPERIMENTAL

Samples with the composition NiO/YSZ = 60/40 wt % were prepared by a modified Pechini method. This particular composition was chosen because it is located above the threshold limit for electron conductance of the anode material. First, an aqueous solution of the metal precursors ($n(M_{\text{tot}}) = 0,05 \text{ mol}$) was mixed by stirring with an appropriate amount of carboxylic acid and ethylene glycol (EG). The initial molar ratios are presented in **Table 1**. The pH of the solution was then adjusted to 8 by bubbling gaseous ammonium through it. The obtained green solution was then heated to approximately 90 °C for 3 h. During this time a considerable amount of water evaporated and the pH of the solution was lowered to a value of around 5. The remaining solution was left overnight in a heating oven at 80 °C. A small part of the as-prepared samples was used for thermal analysis (TG/DTA). The determination of the thermal properties was performed in air at a heating rate 10 °C min⁻¹ on a Netzsch STA 409 thermoanalyzer.

Table 1: Raw materials and their molar ratios used in the synthesis

Tabela 1: Izhodne kemikalije in molska razmerja, uporabljena pri sintezi

Sample	Molar ratio $n(\text{CA}):$ $n(\text{EG}):$ $n(M_{\text{tot}})$	Carboxylic acid (CA)	Metal precursors (M)
CC1	1:1:1	Citric acid	NiCl ₂ · 6H ₂ O (J.T. Baker)
CC2	2:1:1	C ₆ H ₈ O ₇ · H ₂ O (POCH Gliwice)	ZrCl ₄ (Merck-Schuchart)
CC3	3:1:1		Y ₂ O ₃ (Aldrich Chemical Company)
CN2	2:1:1	Citric acid C ₆ H ₈ O ₇ · H ₂ O (POCH Gliwice)	Ni(NO ₃) ₂ · 6H ₂ O (Acros Organics) ZrO(NO ₃) ₂ · xH ₂ O (Acros Organics) Y ₂ O ₃ (Aldrich Chemical Company)
AC2	2:1:1	Ascorbic acid C ₆ H ₈ O ₆ (Riedel de Haën)	NiCl ₂ · 6H ₂ O (J.T. Baker) ZrCl ₄ (Merck-Schuchart) Y ₂ O ₃ (Aldrich Chemical Company)

After drying, the samples were heated up to 300 °C and kept for 1 h at this temperature, which resulted in the formation of a black to dark-grey resin. The obtained resin was thermally treated at different temperatures, and

samples were characterized by X-ray powder diffraction using a Bruker D4 Endeavor instrument with Cu K α radiation ($\lambda = 0.15406 \text{ nm}$). Scanning electron microscopy (Joel T-300 microscope) and a specific surface area determination using the BET method (Micrometrics Gemini 2370 instrument) were used for a further characterisation of the heat pre-treated samples, i.e., calcined at 900 °C for 1 h. The particle size distribution of the powders was determined by laser beam diffraction using a Fritsch Analysette 22.

The sintering behaviour was observed using a Leitz-Wetzlar heating microscope. After the calcination the powders were milled in an agate mortar and uniaxially pressed under 200 MPa into tablets with a 6-mm diameter and heated to 1550 °C at a constant heating rate of 10 °C min⁻¹.

3 RESULTS AND DISCUSSION

Thermal analysis was performed on the samples that were dried in a drying oven at 80 °C overnight. Representative TG and DTA curves of all the studied samples are shown in **Figure 1**.

In almost all the samples (the exception being sample CN2) a continuous (approximately 60 %) loss of weight accompanied by an endothermic effect was observed in the temperature interval from 130 °C to about 400 °C. This thermal effect corresponds to the removal of water⁶, which was formed during polyesterification, and to the loss of ammonium chloride, which sublimates at 335 °C⁷. The large exothermic effect that follows in the temperature range from 400 °C to about 700 °C can be, according to the literature⁶, ascribed to the oxidation of polymeric gel.

A dramatic change in the course of the thermal decomposition was observed for the sample prepared with metal nitrates as precursors (CN2). A large weight loss (83.3 %) was observed up to 300 °C. The first endothermic effect (232 °C) was followed by a very distinct exothermic effect (282 °C). The third thermal effect (exothermic decomposition at 404 °C) was accompanied by a 5 % weight loss up to the final

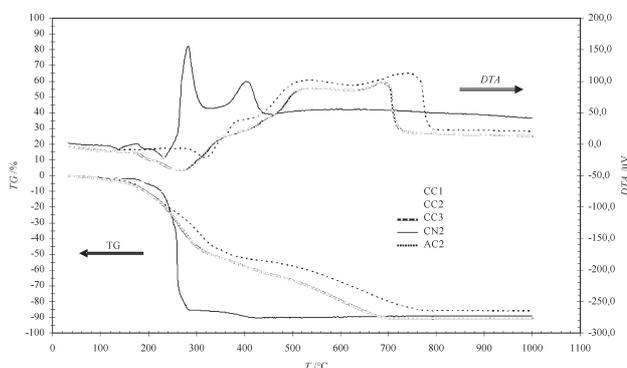


Figure 1: Combined TG-DTA curves of all samples

Slika 1: TG-DTA krivulje vzorcev

temperature at 420 °C. As for the previous samples, it can be assumed that the first endothermic peak corresponds to a dehydration reaction and the two exothermic peaks that follow to the combustion of polymeric gel⁶. The thermal decomposition of the sample is finished at temperatures about 300 °C lower than for samples prepared with metal chlorides as precursors. The difference in the thermal behaviour of this sample from those prepared from metal chlorides can be ascribed to the presence of nitrate ions and their oxidizing properties.

TG/DTA analysis was used to determine the influence of different molar ratios of carboxylic acid and ethylene glycol on the thermal decomposition. By increasing the CA/EG ratio the end temperature of the thermal decompositions was reduced; the thermal decompositions of CC1, CC2, CC3 were finished at 768 °C, 746 °C and 732 °C. The same progressive effect was observed for the DTA analysis; the temperature of the exothermic peak, in the temperature range from 600 °C to 700 °C, increased with the increase of the CA/EG ratio. We assume that because of the higher concentrations of carboxylic acid the thermal effects were larger, which subsequently led to the lowering of the decomposition temperature.

The thermal analysis showed that the majority of samples decomposed in the temperature interval from 700 °C to 780 °C (with the exception of sample CN2). The samples CC1, CC2, CC3 and AC2 were calcined at 700 °C, 800 °C and 900 °C. Representative X-ray diffraction patterns are shown in **Figure 2**. In the materials calcined at 700 °C only nickel oxide was identified. As the temperature of the calcination was increased the peaks of the YSZ phase started to show on the diffractogram. At 900 °C fully crystallized material was obtained, consisting of nickel oxide and zirconium dioxide stabilized with 8 mol % of Y₂O₃.

The thermal decomposition of sample CN2 was finished at 420 °C. The crystallization behaviour was observed at (300, 600, 700, 800 and 900)°C. Full crystallization of the material was achieved at 900 °C. The aluminium peaks in the X-ray diffraction pattern are

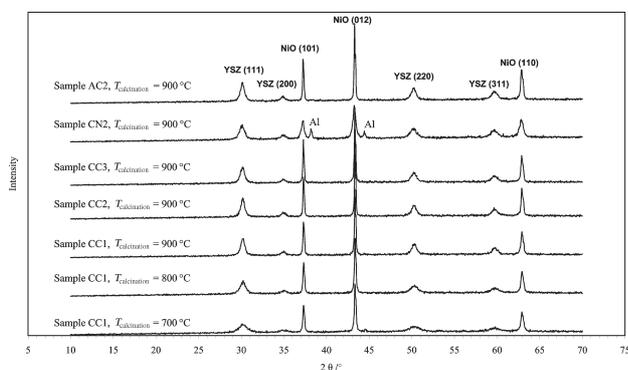


Figure 2: X-ray diffraction patterns of calcined NiO-YSZ powders
Slika 2: Praškovni difraktogrami kalciniranih NiO-YSZ-prahov

present because an aluminium holder was used in the X-ray analysis.

The results of the BET analysis for the powders calcined at 900 °C for 1 h are given in **Table 2**. The use of different molar ratios of citric acid and ethylene glycol and the use of different complexing agents (citric acid and ascorbic acid) had no appreciable influence on the specific surface area of the NiO-YSZ powders. The only exception was the sample prepared with metal nitrates (CN2), the surface area of which was two times higher than the other samples.

Table 2: Specific surface area (S_{BET}) and median particle size (d_{50}) of the calcined samples

Tabela 2: Specifična površina (S_{BET}) in srednja velikost (d_{50}) kalciniranih vzorcev

Sample	$S_{\text{BET}} / (\text{m}^2 \text{g}^{-1})$	$d_{50} / \mu\text{m}$
CC1	12,4	17,1
CC2	11,2	17,3
CC3	15,1	15,3
CN2	28,5	14,1
AC2	17,9	23

Typical SEM photographs of powders calcined at 900 °C for 1 h are shown in **Figure 3**. The morphologies of the NiO-YSZ samples are different in all three cases. Sample CC2 (**Figure 3**, sample *a*) has large irregular agglomerates with a median particle size, determined using laser-beam diffraction, of 17.3 μm (**Table 2**). These irregularly shaped powders were covered with almost spherical particles of 1.3 μm diameter. The material prepared using metal nitrates (**Figure 3**, sample *b*) had almost the same d_{50} (**Table 2**) as sample CC2, but the morphology was different. The particles were porous and did not have a very firm structure; when pressed the material exhibited the lowest green density (**Table 3**). The third sample (**Figure 3**, sample *c*) had the largest median particle size (**Table 2**). Lamellate agglomerates of irregular shapes were covered with nodular particles of 2 μm diameter.

The sintering behaviour of the NiO-YSZ samples was studied using a heating microscope. The linear shrinkage of the samples versus temperature is shown in **Figure 4**. The samples exhibited a linear thermal expansion until about 900 °C. Afterwards, the densification of the samples took place in the temperature range from

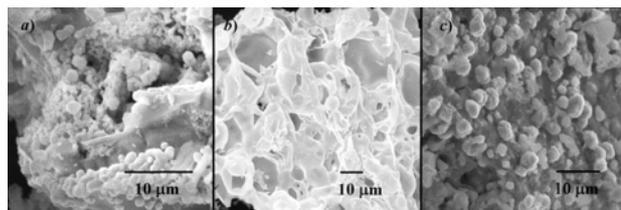


Figure 3: Representative SEM micrographs of samples CC2 (*a*), CN2 (*b*) and AC2 (*c*)

Slika 3: SEM-posnetki vzorcev CC2 (*a*), CN2 (*b*) in AC2 (*c*)

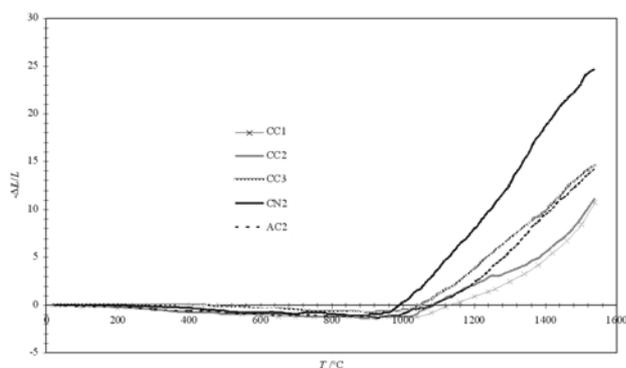


Figure 4: Linear shrinkage versus temperature for calcined powders
Slika 4: Linerni skrčki v odvisnosti od temperature za kalcinirane vzorce

900 °C to 1550 °C. The sintering temperature, relative linear shrinkage and the change of density during the thermal treatment are presented in **Table 3**.

Table 3: Sintering temperature of samples ($T_{\text{sint.}}$), density change and linear dimension changes ($\Delta L/L$) during thermal treatment

Tabela 3: Temperature sintranja vzorcev ($T_{\text{sint.}}$), spremembe gostot in relativni linearni skrčki ($\Delta L/L$) med temperaturno obdelavo

Sample	$T_{\text{sint.}} / ^\circ\text{C}$	$a\rho_{\text{green}} / \%$	$b\rho_{\text{sint.}} / \%$	$\Delta L/L / \%$
CC1	1510	50.6	77.2	13.2
CC2	1510	49.3	75.4	13.2
CC3	1430	49.9	84.4	16.1
CN2	1360	36.4	88.6	25.7
AC2	1340	49.1	82.9	16.0

The results show that with the increase of the CA/EG ratio the sintering temperature was lowered from 1510 °C to 1430 °C. The material with the highest CA/EG ratio achieved 84.4 % of theoretical density. For the sample prepared with metal nitrates as precursors (sample CN2), compared to the samples prepared with metal chlorides as precursors (sample CC2), an appreciable change in the sintering behaviour was observed. The sample exhibited an about 150 °C lower sintering temperature ($T = 1360$ °C) and had the highest percent of relative sintered density (88.6 %) among the examined samples. The lowest sintering temperature (1340 °C) was achieved for the sample prepared with ascorbic acid and metal chlorides as precursors (AC2). But from Figure 4 we can see that the material has a smaller densification capability; the slope of the line in the temperature range from 1100 °C to 1550 °C is lower compared to sample CN2.

4 CONCLUSIONS

Nickel-oxide-yttrium-doped zirconium dioxide (NiO-YSZ) powders were synthesized using a Pechini-

type method. The influence of the synthesis parameters during the thermal treatment and on the specific surface area, the median particle size, the morphology and the sintering behaviour of the products was studied. The increase in the molar ratio of the citric acid and ethylene glycol led to a decrease in the final temperature of the decomposition. The temperature of the sintering was lowered in the case of $n(\text{CA}) : n(\text{EG}) : n(\text{M}) = 3 : 1 : 1$ in spite of the absence of an appreciable difference in the specific surface area. The exchange of metal chlorides for nitrates in the synthesis lowered the final temperature of the thermal decomposition of the sample. The sintering temperature was also lowered and the specific surface area increased to $28 \text{ m}^2\text{g}^{-1}$. The use of ascorbic acid as a complexing agent in the synthesis had no profound effect on the thermal decomposition.

From the results it can be concluded that the highest molar ratio of citric acid to ethylene glycol used in this work and the use of metal nitrates as precursors improved the product characteristics.

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