

BaCe(Ti,Y)O₃ – Ceramic Protonic Conductors for Hydrogen Purification

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Abstract

The aim of this work was to construct the model of electrochemical hydrogen pump and to determine its performance. The influence of titanium and yttrium on physicochemical properties of BaCeO₃ material selected for pump construction was investigated. X-ray diffraction (XRD), differential thermal analysis and termogravimetry (DTA, TG), scanning electron microscopy (SEM) and DC electrical measurements were used as experimental techniques. The introduction of titanium causes an improvement of corrosion resistance against CO_2 and better sinterability [1]. On the other hand, doping by Ti decreased the total and ionic conductivities of the material. Doping by yttrium caused the opposite effect; the increase of electrical conductivity was observed. Basing on the obtained results the optimal composition of the material was selected from the point of view of the construction of electrochemical membrane for hydrogen purification.

Keywords: Protonic conductor, Barium cerate, Hydrogen purification

BaCe(Ti,Y)O₃ – CERAMICZNE PRZEWODNIKI PROTONOWE DO OCZYSZCZANIA WODORU

Celem pracy było zbudowanie modelu elektrochemicznej pompy wodoru i oznaczenie jej osiągów. Zbadano wpływ tytanu i itru na właściwości fizykochemiczne materiału BaCeO₃, wybranego do budowy pompy. Jako techniki eksperymentalne wybrano dyfrakcję promieniowania rentgenowskiego (XRD), termiczną analizę różnicową i termograwimetrię (DTA, TG), skaningową mikroskopię elektronową (SEM) i stałoprądowe pomiary elektryczne. Wprowadzenie tytanu powoduje poprawę odporności na korozję CO₂ i lepszą spiekalność [1]. Z drugiej strony, domieszkowanie Ti zmniejszyło przewodność całkowitą i jonową materiału. Domieszkowanie itrem spowodowało efekt przeciwny - zaobserwowano wzrost przewodności elektrycznej. Opierając się na uzyskanych wynikach wybrano optymalny skład materiału z punktu widzenia zbudowania elektrochemicznej membrany do oczyszczania wodoru.

Słowa kluczowe: przewodnik protonowy, ceran baru, oczyszczanie wodoru

1. Introduction

Production of clean hydrogen is one of the greatest tasks for researchers in the 21^{st} century. The development of effective methods of hydrogen production and purification is still a challenge. One of possible methods is the use of selective membranes based on ceramic protonic conductors such as BaCeO₃, SrCeO₃ or BaZrO₃, modified by different dopants. Electrochemical separation by means membranes is the promising method of production of pure hydrogen. This method is based on ionic transport of hydrogen through the membrane in the form of protons. The membrane separators have not found practical application due to insufficient resistance to CO₂ and humidity in atmosphere and unsatisfactory rate of charge transport through membranes [1].

In this work the Ba(Ce_{1-x}Ti_x)_{1-y}Y_yO₃ material with selected composition (x = 0.05, y = 0.20) was used to prepare two different types of materials for hydrogen separators. One of them was the dense sintered body while the second one was made from the porous Ba(Ce_{1-x}Ti_x)_{1y}Y_yO₃ support. Porous materials were also made using two different methods. The

performance of both types of materials was compared and discussed.

2. Experimental

2.1. Synthesis of material

Powder of Ba(Ce_{1-x}Ti_x)_{1-y}Y_YO₃ (x = 0.05, y = 0.20) was prepared by the solid-state reaction method. Appropriate amounts of barium carbonate BaCO₃ (99.7 %), cerium(IV) oxide CeO₂(99.9 %), TiO₂(99.7 %) nanopowder (all reagents supplied by Aldrich Chemical Company, Inc.) were used as a starting materials. The powder mixture was impregnated with the necessary amount of yttrium nitrate Y(NO₃)·6H₂O water solution, mixed then dried at 80°C, pressed and then calcined at 1200°C for 24 h. The calcination conditions were optimised basing on the DTA&TG and XRD results. The obtained materials were ground in the absolute alcohol suspension using a rotary-vibratory mill (ZrO₂ grinding media).

2.2. Bulk sintered body

The obtained powder was formed in a pellet die $(\phi = 25 \text{ mm})$ at 25 MPa and isostatically pressed at 250 MPa. The body was sintered at 1500°C for 24 h in air atmosphere. Prior to the electrical measurements porous Pt electrodes were screen-printed (Demertron Pt paste) from both sides of the plates and fired at 850°C for 5 minutes. The prepared plates designated for determination of transference numbers were attached on the alumina tube (OD = 8 mm, ID = 5 mm), using the Ceramabond 569 ceramic adhesive to form the electrochemical cell. All prepared samples were stored in the dessicator to avoid any secondary reactions with CO₂ and water vapour before using pellets for further tests and experiments.

2.3. Porous ceramics

Porous ceramics were obtained by two methods:

(i.) "wet" method [2]:

Ba(Ce_{1-x}Ti_x)_{1-y}Y_yO₃ powder, de-mineralised water, agarose, CH₃COOH (2M), Tergitol (TMN 10) were used as substrates. Water suspension of powder was mixed with water solution of agarose (1 wt% in final mixture) at 95°C then 1 g of Tergitol (TMN 10) was added to the mixture. Foam was created by rigorous mechanical mixing, then cooled down using the ice bath to allow gelation. The material was then dried, heated at 600°C for 24 h to remove organic residues, then sintered at T = 1600°C for 6 h.

(ii.) "dry" method:

Ba(Ce_{1-x}Ti_x)_{1-y}Y_yO₃ powder was mixed with 25 vol.% of agarose powder, formed in a pellet die (as in the case of bulk sintered bodies) heated at 600°C for 24 h to remove organic residues, sintered at T = 1600°C for 6 h.



Fig. 1. XRD patterns for perovskite sintered bodies (T = 1200° C for 24 h).

3. Results and discussion

3.1. XRD data

XRD measurements were done using CuK_{α} radiation (Philips X'Pert) within the 20 range 10-90° with the scan rate of 0.008° s⁻¹. Fig. 1 shows the XRD measurements of pellets after sintering at 1500°C for 24 h. Basing on the X-ray diffraction measurements, it was found that material is a single-phase perowskite material. The undoped sample (x = 0) crystallized in orthorhombic (Pmcn structure). The introduction of yttrium and titanium led only to slight changes of the XRD spectra of the samples.

3.2. Microstructure

The SEM observations were made using NOVA NANO SEM scanning electron microscope. The microphotographs were made on powders and freshly prepared fractures, cov-



Fig. 2. SEM microstructure of the BaCeO₃ powder.



Fig. 3. SEM micrograph of the $Ba(Ce_{0.95}Ti_{0.05})_{0.8}Y_{0.2}O_3$ fracture.











f)

h)

Fig. 4. SEM microstructure of porous $Ba(Ce_{0.95}Ti_{0.05})_{0.8}Y_{0.2}O_3$ materials obtained using the "wet" method (a, b, c, d) and the "dry" method (e, f, g, h), both sintered at 1600°C for 6 h.



Fig. 5. The TG results of $Ba(Ce_{1,x}Ti_x)_{1,y}Y_yO_3$ sintered samples before (as-prepared) and after the long-term exposition to the CO_2 -rich atmosphere (7 vol.% of CO_2 for 650 h).

ered by a thin layer of carbon. The example SEM images of powder and of cross section of sintered pellet (at 1500°C for 24 h) are shown in Fig. 2 and Fig. 3).

As it can be seen, the powders with uniform grains with the average sub-micron grain size were obtained. The sintering of materials led to the dense bulk materials with average grain size of few micrometers.

Fig. 4 shows the comparison of porous materials obtained using two different methods: "dry" and "wet". As it can be seen, porous materials obtained by a "dry method" have relatively lower porosity, comparing to the material obtained using the "wet" method. Unfortunately, due to hydrolysis reaction taking place at the stage of preparation, obtaining samples with satisfactory size and shape was difficult. Also, the obtained samples were too small to be used for construction of the model of electrochemical pump for hydrogen pumping.

3.3. Chemical stability against CO₂

One of the limitations in the application of $BaCeO_3$ -based protonic conductors is poor chemical stability against the CO_2 . The possible solution of this drawback, proposed in the literature, is the formation of solid solution with chemically stable compound, e.g. $BaZrO_3$ or $BaTiO_3$ [3]. In this work the material with Ti dopant, proposed previously [3], was used. It was found that introduction of Ti dopant leads to the improvement of chemical stability against CO_2 [3]. The comparison of chemical stability of different materials is shown in Fig. 5. As it can be seen, the samples before tests exhibit only a small weight loss during heating up to 1200°C. This weight loss is smaller than 0.3 % and is caused mainly by the disappearance of protonic defects, accompanied by the water vapour release, as shown in the inset of Fig. 5. After long-term saturation in CO_2 -rich atmosphere, the partial formation of secondary BaCO₃ takes place, which can be observed as liberation of CO_2 during TG measurements. Generally, the higher weight loss the worse chemical stability against CO_2 can be postulated. More details can be found in [3]. Basing on the results presented in Fig. 5 it can be stated that material with the composition $Ba(Ce_{0.95}Ti_{0.05})_{0.8}Y_{0.2}O_3$ exhibited relatively good chemical stability and was selected for further tests.

3.4. Electrical measurements

The DC four-probe electrical conductivity measurements were performed in the temperature range of 773 - 1073 K at atmosphere rich in wet hydrogen H_2 (7 vol.% of hydrogen H_2 in Ar at 100 % RH at T = 25°C).

Transference numbers were calculated using the following formulas [4]:

$$V_{\text{OC}} = \frac{RT}{4F} \left[t_{jon} \cdot \ln \left(\frac{p_{O_2}^{\prime \prime}}{p_{O_2}^{\prime}} \right) - 2t_H \cdot \ln \left(\frac{p_{H_2O}^{\prime \prime}}{p_{H_2O}^{\prime}} \right) \right], \quad (1)$$

$$V_{\rm OC} = \frac{RT}{4F} \left[t_{jon} \cdot \ln \left(\frac{p_{O_2}^{\prime \prime}}{p_{O_2}^{\prime}} \right) - 2t_H \cdot \ln \left(\frac{p_{H_2O}^{\prime \prime}}{p_{H_2O}^{\prime}} \right) \right], \qquad (2)$$

$$t_{jon} = t_H + t_O, (3)$$

$$| = t_{el} + t_{jon}, \qquad (4)$$

where

 V_{oc} – OCV of cell, t_{ion} – ion transference number,

 t_{H} – transference numbers of protons,

 t_0 – transference numbers of oxygen ions,

 t_{el} – transference numbers of electrons.

The required gas compositions were obtained by mixing the gases at a proper ratio, using the MKS gas flow controllers and passing them through a water bubbler. Prior to each measurement, each sample was equilibrated at least 4–5 h under steady conditions [5].

Partial conductivities were calculated as follows:

$$\sigma = t \cdot \sigma_{tot} \tag{5}$$

where:

t – each transference numbers,

 $\sigma-\text{partial}$ conductivity,

 σ_{tot} – total conductivity.

Fig. 6 shows the results of determined partial conductivities for the Ba(Ce_{0.95}Ti_{0.05})_{0.8}Y_{0.2}O₃ sample for hydrogen–rich atmosphere, as a function of temperature. As it can be seen, ionic conductivity is predominant over the electronic conductivity in the whole range of temperatures and can be attributed to the protonic conductivity in the lower temperatures, up to about 650°C. At higher temperatures the increase of both oxygen ion and electronic conductivities can be observed, accompanied by the decrease of protonic conductivity. At the temperature as high as ~820°C the protonic, oxygen



Fig. 6. Partial conductivities of $Ba(Ce_{0.95}Ti_{0.05})_{0.8}Y_{0.2}O_3$ sample as a function of temperature, measured at hydrogen-rich atmosphere (7 vol.% of hydrogen H_2 in Ar at 100 % RH at T = 25°C).

-3.0 Pa B 8 ocv [m v] ц В o 450 P i 8 650 Pa -3 V -5,0 100 200 300 400 Time [min]

дрН<u>_</u> =

3 V

Fig. 8. Changes of OCV of H_2 sensor as a function of time for different applied voltages feeding the electrochemical hydrogen pump. Pump at T = 600°C.

ion and electronic conductivities were found to be almost equal. These results determine the optimal temperature range of the electrochemical hydrogen pump operation to about 600-650°C, where the material may be considered as a protonic conductor.

3.5. Hydrogen pump manufacture and testing

Porous materials were found to be inappropriate for pump construction due to poor mechanical properties and small dimensions of obtained porous bodies. Sintered dense bodies were cut, polished and arranged using ceramic adhesive. Pt electrodes were applied.

Voltage source Keithley SMU 2420, potentiometric H₂ sensor, constructed model of H₂ pump, gas controlling system (MKS Instruments), gas mixtures: Ar + 3.5 % H₂, Ar + 7 % H₂ devices were used to determine the pump tests. The schematic diagram of the used experimental setup is shown in Fig. 7.

Fig. 8 shows the representative results of the tests of hydrogen pumping. The response of the potentiometric hydrogen sensor (Open Cell Voltage – OCV) connected at the outlet of the hydrogen pump, for different applied voltages to the pump, is shown as a function of pump operation time.

As it can be seen the constructed model of hydrogen pump is capable to pump the hydrogen when the voltage is applied using an external source. The increase of calculated,



Fig. 7. Schematic representation of experimental setup used for determination of electrochemical hydrogen pump performance.

based on the measured OCV response of the sensor, generated pressure difference at both sides of the hydrogen pump is in general reversible and follows the increase of applied voltage. The estimated effectiveness of the constructed pump was found to be about 40 %.

4. Conclusions

-2,0

-2*5*

In this work the possibility of construction of a hydrogen electrochemical pump using the $BaCeO_3$ -based protonic conductor was investigated. Different experimental techniques were used to characterize basic properties of obtained materials and to determine electrical propeties of prepared material. Basing on these results the optimal operating conditions were proposed and the performance of hydrogen pumping was tested using the constructed model of electrochemical hydrogen pump. Basing on results of the investigations carried in this work, the following detailed conclusions can be summarised as follows:

- Prepared material crystallized in orthorhombic (Pmcn structure).
- The Ti dopant was used to improve the chemical stability in the presence of CO₂ while the Y dopant was used to improve the total (and mostly protonic) electrical conductivity.
- The attempt to prepare the porous materials was only a partial success, the porous materials with desired porosity were obtained but poor mechanical properties and small size of obtained porous samples limited the preparation of electrochemical pump only to the model based on bulk sintered bodies.
- The estimated efficiency of electrochemical hydrogen pump was found to be about 40 % which is promising for future applications.
- Future work is necessary to increase the electrical conductivity of high-temperature protonic conductors.

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