Comparative Study of BaY₀.1Zr₀.9O₃₋δ Protective Layers Deposited to BaY₀.₁Ce₀.₉O₃₋δ Membrane Using Ultrasonic Spray Pyrolysis and Magnetron Sputtering Methods

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To combine chemical stability of BaY₀(Zr₀.9O₃₋δ (BZY) and good proton conductive properties of BaY₀.₁Ce₀.₉O₃₋δ (BCY) bilayer membranes were prepared. Supportive BCY membranes were prepared applying dry pressing of nanopowder, which was synthesized with ultrasonic spray pyrolysis method. Thin protective BZY coatings were prepared using ultrasonic spray pyrolysis and magnetron sputtering methods. Ultrasonic spray pyrolyzed BZY layers were 0.5–1.1 μm thick, phase pure and with some closed porosity. Protective BZY layers synthesized with reactive magnetron sputtering method were approximately 0.7 μm thick, highly dense and with good phase purity. Activation energy for BCY membrane was 0.35 eV. BZY protective layer sintered at relatively low temperatures (600 to 1150 °C) had minor influence on total activation energy. Sintering at 1350 °C led to a decrease of activation energy of proton transport process at grain boundary region, an increase of activation energy of proton transport in bulk and a slight increase of total activation energy. Sintering at 1350 °C and higher temperatures led to interdiffusion of Zr and Ce cations between BZY and BCY phases and changes in chemical as well as electrochemical properties. Prepared membranes with BZY layer were exposed to CO₂ at 700 °C and were observed to be chemically stable if sintering of BZY were carried out at 1150 °C and lower temperatures.

High temperature proton conductive (HTPC) oxide membranes have a variety of applications, such as hydrogen sensors for detecting hydrogen in gases and in melted metals, detection systems of hydrocarbons in natural gas, devices for hydrogen extraction and precise pumping, reactors for electrochemical hydrogenation, dehydrogenation and production of ammonia etc. Furthermore, these membranes can be used in fuel cells as well as in electrolyzers having some advantages in comparison with oxide ion conductive membranes: a) hydrogen and water are not mixed in fuel cell nor in electrolysis regime and b) higher conductivity and lower activation energy at intermediate temperatures compared with conventional oxide ion conductors.

A variety of different chemical compositions has been tested as potential HTPC oxide membrane materials. For example, Ba-, Sr-, Gd-, La-, and Ca - cerates, zirconates, stannates, niobates and titanates, which are doped with Y, In, Gd, Sm, Sc, Ga (BaCeO₃, BaZr₁₋ₓYₓO₃₋δ, SrZr₁₋ₓYₓO₃₋δ, GdZr₁₋ₓYₓO₃₋δ, La₂₋ₓSrₓCe₀.₉Gd₀.₁O₃₋δ, Gd₂₋ₓLaₓCe₀.₉Gd₀.₁O₃₋δ, Gd₂₋ₓLaₓCe₀.₉Gd₀.₁O₃₋δ). In some studies binary oxides with fluorite-like structure and ternary oxides with pyrochloic structure have been studied as well.

Acceptor doped barium cerate shows the highest protonic conductivities but poor chemical stability. BaCeO₃ and SrCeO₃ are thermodynamically only weakly stabilized and the formation of carbonates takes place in the presence of CO₂. The stability with respect to the formation of carbonates and hydroxides increases in the order of materials: cerate < zirconate < titanate, i.e., opposite to the direction of the increase of stability of protonic defects and as the B site cation electronegativity increases. Some promising results have been achieved to overcome the instability problems with doping the oxide and mixing of different phases, but there is no good solution available yet.

One of the promising approaches for achieving reasonable compromise between chemical stability and conductivity is to prepare a bilayer membrane with well-conductive supportive membrane and with thin chemically stable less conductive layer on top. BaZr₁₋ₓYₓO₃₋δ (BZY) layer on BaCe₁₋ₓYₓO₃₋δ (BCY) electrolyte could be one possible combination of materials with compatible thermomechanical and chemical properties.

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functionality tests for synthesized protective membranes at single cell conditions in the presence of CO\textsubscript{2} have been carried out and the usability of spray pyrolysis for synthesis of BZY is evaluated.

**Experimental**

**Synthesis of supportive BaCe\textsubscript{0.9}Y\textsubscript{0.1}O\textsubscript{3-δ} membrane.**—Stoichiometric amounts of Ba\textsubscript{(NO\textsubscript{3})\textsubscript{2}} (99.95%, Alfa Aesar), Ce\textsubscript{(NO\textsubscript{3})\textsubscript{3}}·6H\textsubscript{2}O (99.99%, Alfa Aesar), and Y\textsubscript{(NO\textsubscript{3})\textsubscript{3}}·6H\textsubscript{2}O (99.9%, Alfa Aesar) were dissolved in deionized water (Milli-Q) whereby the concentration of Ba\textsuperscript{2+} in the solution was 2.5·10^{-3} M. The solution was nebulized with ultrasonic particle generator (Sonaer Model 241) applying 2.4 MHz ultrasonic frequency and introduced to the tubular furnace with two hot zones. In the first zone at 600 °C the generated aerosol of salt solution was dried and decomposed partially. In the second zone at 900 °C the salt powder decomposed and reacted mostly to composite oxide. Formed oxide powder was collected to the filter and calcined at 900 °C to finish the formation of complex oxide. Afterwards the deagglomeration was carried out in isopropanol. Particle size distribution of the powder was obtained using Microtrac S3500 Bluewave particle size analyzer. Dried powder was pressed to pellets with 11 mm diameter using 40 kN force. Optimal programme for membrane sintering was 3 °C/min heating up to 400 °C, subsequently the temperature was raised to 1500 °C with speed 7 °C/min, where temperature was held constant for 30 h and then decreased to room temperature 2 °C/min. Sintering of membranes was carried out between porous pellets of BaCe\textsubscript{0.9}Y\textsubscript{0.1}O\textsubscript{3-δ}. Electrochemical characterization was performed in the atmosphere of humidified mixtures of Ar and H\textsubscript{2} (5:95) using Solartron 1287A potentiostat/galvanostat electrochemical interface. Permeation measurements were carried out using a Solartron 1260 FRA in conjunction with a Solartron 1287A potentiostat/galvanostat electrochemical interface.

**Preparation of BaZr\textsubscript{0.9}Y\textsubscript{0.1}O\textsubscript{3-δ} layer using ultrasonic spray pyrolysis method.**—Thin oxide films were prepared using solutions made from BaCl\textsubscript{2}·2H\textsubscript{2}O (Alfa Aesar, 99.999%), Zr\textsubscript{(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{4}} (Sigma Aldrich, 98%) and YCl\textsubscript{3}·6H\textsubscript{2}O (Sigma Aldrich, 99.99%) with stoichiometric proportions. For all salts the content of crystal water was controlled implementing thermal analysis in oxidizing conditions. Diethylene glycol butyl ether (Sigma Aldrich, >99.2%) was used as organic co-solvent in proportional amount with water. Yttria stabilized zirconia (Kerafol) and yttrium doped barium cerate substrates were used during the optimization of deposition parameters and for the preparation of membranes, respectively.

The precursor solutions for ultrasonic spray deposition were prepared by dissolving (Precisa XB 220A) salts in Milli-Q water and then adding organic solvent to obtain 0.1M solution. Thereafter the constant stirring for 24 hours was applied.

Prepared solution was sprayed onto substrate with ultrasonic atomizer working at 2.4 MHz frequency (Sonaer 241PG ultrasonic particle generator). Substrate was heated on the melted mixture of Pb and Sn metals (for uniform heating) using electrical heater (IKA C-MAG 4). Deposition was carried out applying 60 second long spraying cycles alternately with 60 second long thermal stabilization steps. Sprayed thin raw as well as thermally treated films were characterized using scanning electron microscope (Zeiss EVO MA 15) and diffractometer (Bruker D8 Advanced). Electrochemical measurements were carried out using a Solartron 1260 FRA in conjunction with a Solartron 1287A potentiostat/galvanostat electrochemical interface.

Thermogravimetric and differential calorimetric analysis of salt decomposition was conducted with NETZSCH STA 449 F3 Jupiter applying heating rate 10 °C/min and total gas flow rate 60 ml/min in different gas environments (100% N\textsubscript{2} and 79% N\textsubscript{2} + 21% O\textsubscript{2}).

**Preparation of BaZr\textsubscript{0.9}Y\textsubscript{0.1}O\textsubscript{3-δ} layer with magnetron sputtering method.**—BZY layer was deposited using AJA International UHV magnetron sputtering system applying the following parameters: base vacuum 10^{-9} Torr, 8 mTorr Ar + O\textsubscript{2} pressure (Ar 50 ml/min, O\textsubscript{2} 5 ml/min), sample temperature 250 °C, 15 W bias at the sample, 4 h 40 min deposition time and 18 cm distance from targets to the substrate.

Reactive sputtering was carried out using simultaneously Zr\textsubscript{0.9}Y\textsubscript{0.1} (>99.9 %, AJA International) and Ba (99.5 %, AJA International) targets with 7.62 cm diameter applying 170 W pulsed direct current (3 μs, 100 kHz) and 150 W radio frequency (RF) sources, respectively.

**Results and Discussion**

**Preparation of supportive BaCe\textsubscript{0.9}Y\textsubscript{0.1}O\textsubscript{3-δ} membrane.**—Supportive BCY membranes used in this study were synthesized as described in detail in the previous section of this paper using nanopowder prepared with ultrasonic spray pyrolysis (SP) method. As it can be seen from Figure 1, the grain size of sintered membrane varied from 1 to 3 μm. The thickness of the membranes after sintering at 1500 °C and polishing of surfaces was approximately 300 μm. Good phase purity and orthorhombic perovskite structure of BCY was confirmed with XRD analysis (Fig. 2). BCY layers with various thicknesses were synthesized onto those supporting BCY membranes (Fig. 3) with spray pyrolysis and magnetron sputtering methods.

**Preparation of protective BaZr\textsubscript{0.9}Y\textsubscript{0.1}O\textsubscript{3-δ} layer using reactive magnetron sputtering.**—Detailed technical information about reactive magnetron sputtering is presented in the Experimental section of this paper. Phase pure layer (Fig. 4) was obtained only at certain range of target power values. The average crystallite size and unit cell parameter of as deposited layer were 4.9 nm and 4.26 Å, respectively. Annealing of prepared layer at 600 °C during 50 hours led to a decrease of average unit cell parameter from 4.26 to 4.20 Å and an increase of average crystallite size from 4.9 nm to 8.8 nm (Fig. 4). Identical
behavior was observed when BZY layer was deposited to the BCY substrate. At both cases, at sapphire and at BCY, the epitaxial effect was not observed, most likely because of relatively low deposition temperature. Average thickness of as-deposited layer was approximately 0.7 μm (Fig. 5). The thickness of layer did not change during annealing process, which indicates the high density of as-deposited layer.

Preparation of protective BaZr_{0.9}Y_{0.1}O_{3-δ} layer using ultrasonic spray pyrolysis method.—Initial stage of optimization of layer preparation parameters using spray pyrolysis method was carried out on YSZ substrates because of better availability compared to BCY. Obtained deposition parameters were then slightly modified and transferred to prepare layers to BCY. As it can be seen from figure 7a, the spray pyrolyzed raw layer deposits were homogenous and approximately 1.1 μm thick with some surface roughness. Sintering at 1150°C led to thinner BZY layer (~0.5 to 0.7 μm) (Figure 7b) compared to raw layer, which was most likely caused by decomposition of some residual carbonaceous compounds. The grain size of BZY was after sintering at 1150°C approximately 110 nm and increased when sintering temperature was increased to 1350°C. At both layers some closed porosity could be observed (Figs. 7b and 7c). XRD results of BZY on BCY after sintering at 1150°C indicate that the unit cell parameters were very close to theoretical reference values and similar to unit cell parameters obtained for BZY when magnetron sputtered BZY at sapphire was annealed at 600°C. An increase of BZY unit cell parameters was observed when sintering temperatures higher than 1150°C were applied (Table I). Increase of unit cell parameters in BZY layer because of sintering at temperatures higher than 1150°C is very likely caused by interdiffusion of Ce and Zr between BZY and BCY phase and substitution of Zr^{4+} (0.72 Å) by Ce^{4+} (0.87 Å) in BZY layer. This phenomenon was also confirmed by the results of TOF-SIMS analysis obtained for cross-sections of BCY/BZY membranes sintered at high temperatures. At lower temperatures than 1150°C active interdiffusion was not observed. These results are in good accordance with Fabbri et al. who found that at 1100°C there is no segregation of BZY and BCY phases.

Stability tests at differently synthesized and treated BZY layers at 700°C in CO₂ atmosphere were carried out. The formation of BaCO₃ and CeO₂ crystals was detected when BCY or BCY with BZY layer on top sintered at 1350°C were used. When BZY were sintered at 600°C or 1150°C, the formation of BaCO₃ and CeO₂ was not observed. This behavior confirms the chemical stability of BZY layer in CO₂ atmosphere if BZY and BCY phases are not mixed. Based on these experiments it can be accentuated that sintering of BZY on top of BCY at higher temperatures than 1150°C is not possible without the loss of BZY properties.

Electrochemical characterization of differently synthesized BZY layers on supportive BCY.—Electrochemical properties of BCY/BZY membranes were characterized using impedance spectroscopy. The bulk phase resistance R_{bulk} and total resistance R_{tot} values were determined using extrapolation of high frequency semicircle of Nyquist plot (Fig. 8). The shape and size of the semicircle did not depend on electrode polarization, which indicates that the processes characterized by this semicircle do not take place in Pt electrode and in three phase boundary of Pt electrode, gas phase and electrolyte and as accepted in literature are characteristic for processes at grain boundary interfaces and bulk phase (Fig. 8). Grain boundary resistance R_{gb} was obtained by subtraction of R_{bulk} from R_{tot} value. The
Figure 7. SEM image of cross-section of spray pyrolyzed BaZr0.9Y0.1O3-δ layer before (a) and after sintering at 1150°C (b) and 1350°C (c).

Table I. Dependence of unit cell parameters of BZY (deposited onto BCY) on sintering temperature.

<table>
<thead>
<tr>
<th>Phase</th>
<th>d_1 (1150°C)</th>
<th>d_2 (1250°C)</th>
<th>d_3 (1350°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaY0.1Zr0.9O3-δ(1,0,0)</td>
<td>4.197</td>
<td>4.204</td>
<td>4.213</td>
</tr>
<tr>
<td>BaY0.1Zr0.9O3-δ(1,1,0)</td>
<td>2.968</td>
<td>2.973</td>
<td>2.979</td>
</tr>
<tr>
<td>BaY0.1Zr0.9O3-δ(1,1,1)</td>
<td>2.424</td>
<td>2.427</td>
<td>2.432</td>
</tr>
<tr>
<td>BaY0.1Zr0.9O3-δ(2,0,0)</td>
<td>2.098</td>
<td>2.102</td>
<td>2.107</td>
</tr>
<tr>
<td>BaY0.1Zr0.9O3-δ(2,1,0)</td>
<td>1.877</td>
<td>1.880</td>
<td>1.884</td>
</tr>
<tr>
<td>BaY0.1Zr0.9O3-δ(2,1,1)</td>
<td>1.714</td>
<td>1.716</td>
<td>1.720</td>
</tr>
<tr>
<td>BaY0.1Zr0.9O3-δ(2,2,0)</td>
<td>1.484</td>
<td>1.488</td>
<td>1.490</td>
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</tbody>
</table>

Figure 8. Extrapolation of high frequency semicircle of Nyquist plot to obtain total resistance $R_{tot}$ and bulk phase resistance $R_{bulk}$ values.
well-known phenomenon and has also been studied in details in the case of BZY. Slightly higher specific conductivity was obtained for BZY layers deposited using SP and MS methods which is most likely caused by the smaller average thickness of MS layers compared to SP layers. It could be concluded, that BZY layers deposited using SP and MS methods have only minor influence on the total conductivity of BCY/BZY bilayer membrane if particular BCY membranes are used.

Conclusions
Proton conductive BaCe0.9Y0.1O3-δ membranes were prepared based on the nanopowders, which were synthesized using spray pyrolysis method. Sintering of BaCe0.9Y0.1O3-δ was optimized and a possibility of sintering at 1400 °C to achieve homogeneous membrane was demonstrated. However, the best electrochemical performance was observed when BCY membranes were sintered at 1500 °C. Chemically stable BaZr0.9Y0.1O3-δ layers were deposited to the supportive BaCe0.9Y0.1O3-δ membrane using ultrasonic spray pyrolysis and magnetron sputtering methods. Activation energy and total conductivity depended on the synthesis method and sintering program, i.e. preparation method is higher. Quality is better compared to SP but technical complexity of BCY with MS BZY layer compared to BCY with SP BZY layer, which is most likely caused by the smaller average thickness of MS layers compared to SP layers. It could be concluded, that BZY layers deposited using SP and MS methods have only minor influence on the total conductivity of BCY/BZY bilayer membrane if particular BCY membranes are used.

Acknowledgments
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Table II. Activation energies characteristic for processes at temperature range from 550°C to 650°C and specific conductivities at 600°C.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>E_a,bulk (eV)</th>
<th>E_a,gb (eV)</th>
<th>E_a,tot (eV)</th>
<th>σ (S cm⁻¹)</th>
</tr>
</thead>
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<tr>
<td>BCY</td>
<td>0.35</td>
<td>0.34</td>
<td>0.35</td>
<td>1.6·10⁻³ (600°C)</td>
</tr>
<tr>
<td>BCY with MS BZY (600°C)</td>
<td>0.25</td>
<td>0.29</td>
<td>0.35</td>
<td>1.7·10⁻³ (600°C)</td>
</tr>
<tr>
<td>BCY with SP BZY (1150°C)</td>
<td>0.33</td>
<td>0.59</td>
<td>0.35</td>
<td>1.4·10⁻³ (600°C)</td>
</tr>
<tr>
<td>BCY with MS BZY (1350°C)</td>
<td>0.36</td>
<td>0.33</td>
<td>0.36</td>
<td>1.7·10⁻³ (600°C)</td>
</tr>
<tr>
<td>BCY with SP BZY (1350°C)</td>
<td>0.39</td>
<td>0.26</td>
<td>0.36</td>
<td>1.1·10⁻³ (600°C)</td>
</tr>
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