DIACRYLOYL DERIVATIVE OF MANNITOL – SYNTHESIS AND APPLICATION IN GELCASTING OF $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ COMPOSITES

The aim of research was the elaboration of the synthesis of new organic monomer applicable in gelcasting. The substance named 3,4-di-acryloyl-D-mannitol which contains two acryloyl groups and four hydroxyl groups in its molecule has been synthesized. The monomer has been then applied in the preparation of $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ composites by gelcasting and subsequent sintering. Rheological properties of ceramic suspensions have been examined, as well as the properties of green and sintered bodies. SEM observations allowed to determine the distribution of zirconia grains in alumina matrix. Density, Vickers hardness and fracture toughness of ZTA composites have been measured. The new monomer, that is diacryloyl derivative of mannitol, is less sensitive to the oxygen inhibition than commonly used in gelcasting and commercially available 2-hydroxyethyl acrylate.

Keywords: gelcasting, ZTA, composites, zirconia, mannitol

1. Introduction

Ceramic materials are of high interest due to their unique properties such as high hardness, high mechanical strength, chemical and wear resistance, considerable dielectric properties, etc. The research in the field of ceramics are focused mainly on the development of new methods of synthesis of ceramic powders (including nanopowders) [1-3], through optimization of shaping techniques [4-6] up to research on advanced sintering methods and characterization of the obtained materials [7-9]. Shaping of ceramic powders requires the use of various organic additives which enable or facilitate moulding of powders into desired shape. Among these processing agents the following additives can be mentioned: dispersing agents (deflocculants), binders, plasticizers, organic monomers together with activators and initiators of polymerization, pore-formers, surfactants, etc. [10-13]. The selection of suitable additives depends on the shaping method. In recent decades, much research is devoted to gelcasting which is a pressureless shaping method based on colloidal processing. Gelcasting consists of polymerization reaction which takes place in situ that is in a ceramic suspension, thus the created polymeric network holds ceramic particles together in the desired shape [14-16]. The key role in gelcasting is played by the selection of organic monomers which have positive influence on rheological properties of ceramics suspensions and create a strength gel. There are commercially available monomers such as acrylamide or 2-hydroxyethyl acrylate but they are characterized by the excessive toxicity (especially acrylamide) or are sensitive to the so called oxygen inhibition which slow down the polymerization reaction [17]. Moreover, commercially available monomers are often used together with the so called cross-linking agents what increases the total content of organics in the green body [18]. Although the addition of cross-linking agent seems not to be large in comparison to other organic additives [19] but thinking about the possibility of implementation of gelcasting to industrial low-tonnage production any reduction of the organics content will be beneficial. Moreover, according to research made by Bednarek and Szafran [20] during thermal decomposition of N,N'-methylenebisacrylamide (the most often used cross-linking agent in gelcasting) NO and NO$_2$ oxides are released to the atmosphere what is harmful from the environmental point of view. Therefore, there appeared recently research focused on the synthesis of organic monomers and use of new type of processing agents which would facilitate the gelcasting process and have the positive influence on the properties of green and sintered bodies [21,22].

Taking into consideration the above aspects, the aim of the research was to elaborate the synthesis of new monomer which would fulfil the following requirements: low-toxicity, water-solubility and lower sensitivity to the oxygen inhibition in comparison to commercially available 2-hydroxyethyl acrylate. The proposed monomer was based on D-mannitol (sugar alcohol) and contained two acryloyl groups in a molecule. The synthesized substance has been then used in the preparation of $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ composites by gelcasting and subsequent sintering. ZTA composites have been chosen in order to examine the influence...
of gelcasting on the homogeneity of the distribution of zirconia in alumina matrix. Although the properties of ZTA composites are intensively studied by many research groups [23-27], the application of gelcasting in shaping of alumina-zirconia samples may open up new possibilities of obtaining elements of complicated geometry. Alumina-zirconia composites combine the advantageous features of Al$_2$O$_3$ (high Young modulus and hardness) and ZrO$_2$ (notable fracture toughness and bending strength). Currently Al$_2$O$_3$-ZrO$_2$ composites are used as cutting tools, bearings, bushings and screws.

2. Experimental

2.1. Synthesis of 3,4-di-O-acryloyl-D-mannitol

The synthesis of 3,4-di-O-acryloyl-D-mannitol is a III stage process. It has been elaborated on the basis of the previous experience of the Co-authors research team in which the substances such as 3-O-acryloyl-D-glucose, 1-O-acryloyl-D-fructose and 6-O-acryloyl-D-galactose have been obtained [28-30]. The reagents for the organic synthesis have been purchased from the following suppliers: D-mannitol (POCh, Poland, puriss), anhydrous acetone (POCh, Poland, puriss), anhydrous ZnCl$_2$ (POCh, Poland, puriss), acryloyl chloride (Sigma-Aldrich, 96%), dichloromethane (Sigma-Aldrich, anhydrous, $\geq 99.8\%$), triethylamine (Sigma-Adlrich, 99.5%), diethyl ether (Sigma-Aldrich, anhydrous, $\geq 99.7\%$), phenothiazine (Sigma-Aldrich, $\geq 98\%$), K$_2$CO$_3$ (POCh, Poland, puriss), MgSO$_4$ (POCh, Poland, puriss), H$_2$SO$_4$ (POCh, Poland, puriss), PbCO$_3$ (POCh, Poland, puriss).

The scheme of the synthesis of 3,4-di-O-acryloyl-D-mannitol is shown in Fig. 1.

Stage I: Synthesis of 1,2:5,6-di-O-isopropylidene-D-mannitol (DIPM)

The synthesis of 1,2:5,6-di-O-isopropylidene-D-mannitol has been performed on the basis of the procedure described by Alvarenga et al [31] and Yokoyama et al. [32]. In the round-bottom flask 47 g of ZnCl$_2$ has been placed and then melted over the burner. The flask was then closed with calcium chloride tube. After cooling 300 ml of acetone was added. The magnetic stirrer was switched on and the ice and salt bath was set. Then 30 g of D-mannitol was added at 0°C. The ice bath was removed and the whole mixture was stirred at room temperature for 24 hours. The reaction was terminated by the addition of 48 g of K$_2$CO$_3$ in water at 0°C. The precipitate was filtered off under reduced pressure. The filtrate was concentrated with diethyl ether (4 x 100 ml). The combined organic phases were dried by using anhydrous MgSO$_4$. Then the solvent was evaporated and pure 1,2:5,6-di-O-isopropylidene-D-mannitol (DIPM) was obtained. Reaction yield was 82%. The purity was checked by $^1$HNMR spectrum in CDCl$_3$.

$^1$HNMR (CDCl$_3$): 4.17-4.21 (m, 2H, C$_2$), 4.12 (dd, J = 6.4, 8.5 Hz, 2H, C1), 3.97 (dd, J = 5.6, 8.5 Hz, 2H, C1), 3.74 (bt, 2H, C3), 2.56 (d, J = 6.6 Hz, OH), 1.42 (s, 6H, 2xCH$_3$), 1.36 (s, 6H, 2xCH$_3$).

Stage II: Synthesis of 3,4-di-O-acryloyl-1,2:5,6-di-O-isopropylidene-D-mannitol (ACR-DIPM)

DIPM (50 g), triethylamine (80 ml), phenothiazine as a stabilizer (0.5 g) and dichloromethane (500 ml) were placed in a three-neck round-bottom flask. At 0°C acryloyl chloride (40.5 ml) was added dropwise with stirring. After the addition of the acryloyl chloride, the bath was removed and stirring was continued at reflux for 6 hours. Then, distilled water and dichloromethane were added and two phases have been separated. The aqueous phase was extracted with dichloromethane. The combined organic phases were washed with 5% H$_2$SO$_4$ and water and then dried by using anhydrous MgSO$_4$. After filtering off the drying agent, the mixture was placed in a rotary evaporator at 25°C. The resulting oil was dissolved in hot pentane and boiled with activated carbon. After filtration the impurities the mixture was stripped to dryness on a rotary evaporator to give 3,4-di-O-acryloyl-1,2:5,6-di-O-isopropylidene-D-mannitol (ACR-DIPM) as a dark oil. Reaction yield was 86%. Purity (confirmed by $^1$HNMR spectrum) is sufficient for further synthesis.

$^1$HNMR (CDCl$_3$): 6.46 (dd, J = 1.5, 17 Hz, 2H, H$_2$C=C), 5.15 (dd, J = 10, 17 Hz, 2H, C=CH), 5.91 (dd, J = 1.5, 10 Hz, 2H, H$_2$C=C), 5.44 (d, J = 5.5 Hz, 2H, C3), 4.20-4.24 (m, 2H, C2), 3.94 (dd, J = 6.5, 8.5 Hz, 2H, C1), 3.88 (dd, J = 6.0, 8.5 Hz, 2H, C1), 1.35 (s, 6H, 2xCH$_3$), 1.31 (s, 6H, 2xCH$_3$).

Fig. 1. Scheme of the synthesis of 3,4-di-O-acryloyl-D-mannitol (ACR-MAN)
Stage III: Synthesis of 3,4-Di-O-acryloyl-D-mannitol (ACR-MAN)

ACR-DIPM (56 g) in 0.02 M H₂SO₄ (500 ml) was heated for 4h in an oil bath, keeping the reaction temperature at 60°C. The mixture was then cooled to room temperature and lead carbonate (9.2 g) was added. The suspension was stirred for 1h at room temperature, then filtered and concentrated on a rotary evaporator at 30°C. Yellow ACR-MAN aqueous solution (19%) was obtained. Reaction yield was 58%. The chemical structure was confirmed by ¹H NMR.

¹H NMR (D₂O): 6.49 (dd, J = 1.0, 17.5 Hz, 2H, H 2C=C), 6.22 (dd, J = 10.5, 17.5 Hz, 2H, C=CH), 6.05 (dd, J = 1.0, 10.5 Hz, 2H, H₂C=C), 5.41 (d, J = 7.5 Hz, 2H, C₃), 3.84-3.88 (m, 2H), 3.67-3.71 (m, 2H), 3.54-3.58 (m, 2H).

The influence of the new ACR-MAN monomer on the selected properties of ceramic suspensions, green and sintered bodies has been then examined.

2.2. Gelcasting of Al₂O₃-ZrO₂ composites

2.2.1. Materials

The ceramic powders used in gelcasting process were as follows: α-Al₂O₃, TM-DAR (Taimei Chemicals, Japan) of mean particle size D₅₀ = 100 nm, specific surface area 11.5 m²/g measured by BET on ASAP 2020 V3.01H (Micromeritics, USA), density 3.98 g/cm³ measured by helium pycnometer on AccuPyC II 1340 Pycnometer (Micromeritics, USA) and yttria stabilized zirconia TZ-PX-245 (Tosoh Corporation, Japan) of mean particle size D₅₀ = 40 nm, specific surface area 13.2 m²/g and density 5.86 g/cm³. Diammonium hydrocitrate, DAC (POCh, Poland, puriss) was used as dispersing agent. N,N,N',N'-tetramethylethylenediamine, TEMED (Fluka, >98%) played the role of activator and ammonium persulfate (Aldrich, ≥98%), used in the form of 1 wt% aqueous solution, was the initiator of radical polymerization. Deionised water was used as a solvent. The synthesized 3,4-di-O-acryloyl-D-glucose, ACR-MAN has been used as the organic monomer. Additionally, commercially available 2-hydroxyethyl acrylate, HEA (Fluka, >97%) was used as a comparative monomer.

Al₂O₃-ZrO₂ aqueous suspensions with investigated monomers were prepared in deionised water at room temperature. At first, the dispersing agent was dissolved in water followed by the monomer and the activator. The composition of prepared ceramic suspensions is given in Table 1. Al₂O₃ and ZrO₂ powders have been then added and the suspensions were mixed in an alumina jar in a planetary ball mill PM100 (Retsch) for 60 minutes with a speed of 300 rpm. Thereafter, the slurries have been mixed and degassed in a Thinky Are-250 Mixing and Degassing Machine for 2 × 4 minutes with a speed of 800 rpm (mixing) and 1800 rpm (degassing). The equipment allows to remove bubbles >1 μm. After that, the initiator of polymerization was added and the slurries were mixed for additional 1 minute. Slurries with applied monomers are able to gelate at room temperature. The mixture was then cast into PVC moulds of internal diameter 20 mm and height 5 mm. After a thick gelled bodies were obtained, specimens were unmoulded and dried for 24 hours at 50°C. The sintering process of ceramic samples obtained by gelcasting was then conducted in Carbolite furnace in air (1550°C / 1 h).

Sintered bodies have been polished on Buehler grinder-polisher MetaServ 250 before hardness measurements and SEM observations. Vickers indentations have been done on Digital Vickers Hardness Tester HVS-30T (Huatec Group Corporation) applying the load of 98 N. Five indentations were made for each sample. The measurements of the diagonals and cracks have been done on Nikon light microscope. The fracture toughness has been calculated with the use of Niihara equation. The samples have been thermally etched at 1450°C for 15 minutes prior to SEM observations. SEM images of green bodies and obtained ZTA composites were done on Ultra Plus (Zeiss).

Rheological properties of ceramic suspensions without the addition of the initiator of polymerization were determined on Kinexus Pro rheometer (Malvern Instruments) in the parallel plate geometry with a gap of 0.5 mm. The shear rate increased from 0.1 to 100 s⁻¹ and decreased back to 0.1 s⁻¹. The density of samples was measured by Archimedes’ method in kerosene and water, respectively for green and sintered bodies.

<table>
<thead>
<tr>
<th>Suspension No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ [vol %]</td>
<td>55</td>
<td>50</td>
<td>45</td>
<td>40</td>
<td>35</td>
<td>0</td>
<td>55</td>
<td>50</td>
<td>45</td>
<td>40</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>ZrO₂ [vol %]</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>40</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>DAC [wt %]*</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>ACR-MAN [wt %]*</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HEA [wt %]**</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TEMED [wt %]**</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>APS [wt %]**</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

* with respect to ceramic powders content
** with respect to monomers content
3. Results and discussion

The concentration of the ZrO₂ in alumina-zirconia slurries equaled 5-20 vol %, while the total solid loading was 55 vol % (Table 1). In case of suspensions composed of pure ZrO₂, the solid loading was 40 vol % because of higher density of zirconia than alumina.

At first, rheological properties of suspensions have been measured. Fig. 2 presents the exemplary viscosity curves of the slurries containing 40 vol % of Al₂O₃ and 15 vol % of ZrO₂ and respectively ACR-MAN and HEA monomers.

Both slurries exhibited shear thinning behaviour. However, in case of the suspension containing ACR-MAN, the rapid decrease of the viscosity at low shear rates (0.1-1 s⁻¹) was observed. It is the beneficial feature, because higher viscosity of the slurry at a standstill may prevent the so-called oxygen inhibition which is the undesired phenomenon in gelcasting. Oxygen diffusion through highly viscous suspension is hindered and, as the result, the polymerization reaction is not disturbed.

Suspensions containing HEA were characterized by ten times lower viscosity than suspensions containing ACR-MAN. It can be therefore concluded that the presence of the second acryloyl group in the monomer molecule influences on the increase of the ceramic slurries viscosity, while the presence of four hydroxyl groups ensures water-solubility of ACR-MAN. However, the suspensions containing ACR-MAN were still fluid enough to fill precisely the PVC moulds.

For the obtained green bodies the density has been measured (Table 2). The density of the samples containing Al₂O₃ and ZrO₂ powders was high and equaled 56-59% of theoretical density. No significant differences between both monomers have been observed. The density of samples made of pure zirconia was lower (48-49%) because the concentration of solid phase in suspensions equaled 40 vol %.

<table>
<thead>
<tr>
<th>Property</th>
<th>Relative density of green body [%]</th>
<th>Relative density of sintered body [%]</th>
<th>Linear shrinkage after sintering [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Al₂O₃ (ACR-MAN)</td>
<td>59.6</td>
<td>97.9</td>
<td>16.5</td>
</tr>
<tr>
<td>100% Al₂O₃ (HEA)</td>
<td>59.2</td>
<td>97.9</td>
<td>16.6</td>
</tr>
<tr>
<td>ZTA – 5% ZrO₂ (ACR-MAN)</td>
<td>58.3</td>
<td>97.7</td>
<td>17.3</td>
</tr>
<tr>
<td>ZTA – 5% ZrO₂ (HEA)</td>
<td>57.4</td>
<td>97.5</td>
<td>17.0</td>
</tr>
<tr>
<td>ZTA – 10% ZrO₂ (ACR-MAN)</td>
<td>59.2</td>
<td>98.1</td>
<td>17.0</td>
</tr>
<tr>
<td>ZTA – 10% ZrO₂ (HEA)</td>
<td>57.9</td>
<td>97.9</td>
<td>17.0</td>
</tr>
<tr>
<td>ZTA – 15% ZrO₂ (ACR-MAN)</td>
<td>56.9</td>
<td>97.1</td>
<td>17.3</td>
</tr>
<tr>
<td>ZTA – 15% ZrO₂ (HEA)</td>
<td>56.9</td>
<td>97.3</td>
<td>17.4</td>
</tr>
<tr>
<td>ZTA – 20% ZrO₂ (ACR-MAN)</td>
<td>58.6</td>
<td>97.7</td>
<td>17.2</td>
</tr>
<tr>
<td>ZTA – 20% ZrO₂ (HEA)</td>
<td>57.5</td>
<td>97.8</td>
<td>17.2</td>
</tr>
<tr>
<td>100% ZrO₂ (ACR-MAN)</td>
<td>43.3</td>
<td>100.0</td>
<td>20.5</td>
</tr>
<tr>
<td>100% ZrO₂ (HEA)</td>
<td>49.3</td>
<td>99.7</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Fig. 2. Viscosity curves of the Al₂O₃ (40 vol %) + ZrO₂ (15 vol %) suspensions based on two monomers: ACR-MAN and HEA.
The SEM images (Fig. 3) show high homogeneity of both samples in a green state. The images confirm also that the samples are characterized by high green density. Additionally, in case of sample containing polymer derived from HEA, polymeric bridges between ceramic particles could be observed, what has been marked with red colour. The bridges have been not observed in samples containing polymer derived from ACR-MAN. It means that the polymer may surround the particles what is difficult to be observed under SEM.

The biggest difference between both polymers (derived from ACR-MAN and HEA after gelcasting process) was observed during preliminary bending tests. Strong exfoliation was observed for samples made of HEA (Fig. 3b) what could be the result of oxygen inhibition which restrained the polymerization at the top part of the sample [19]. The problems with exfoliation have been not observed in case of ARC-MAN (Fig. 3a).

For the sintered samples the measurement of the relative density, linear shrinkage, Vickers hardness, fracture toughness $K_{IC}$ and microstructure observations have been performed. The relative density of sintered bodies containing $\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$ grains equaled 97-98% of theoretical density. The highest density (100%) was observed for pure zirconia ceramics. The used TZ-PX-245 zirconia powder due to the presence of $\text{Y}_2\text{O}_3$, HfO$_2$ and other oxides undergoes sintering easier than highly pure TM-DAR alumina (purity 99.99%). This is due to the possibility of appearance of liquid phase during sintering process. Therefore, the relative density of zirconia samples equals 100% (what confirms also SEM image) and the density of samples containing alumina is a little lower.

The highest linear shrinkage (20%) was also observed for pure zirconia. This can be explained by the fact that the $\text{ZrO}_2$ green bodies were characterized by the lowest density.

SEM observations (Fig. 4) revealed the interesting aspects which can be linked with the properties of sintered bodies. The biggest grain growth was observed for pure alumina samples. Additionally, grinding and polishing (despite optimization of the procedure) caused that some grains have been pulled out of the material. This phenomenon has been observed mainly in case of $\text{Al}_2\text{O}_3$ samples. It can be explained by the fact that highly pure alumina powder was used what resulted in weak grain boundaries after sintering process. In case of ZTA samples it can be noticed that the higher content of the zirconia, the lower the grain growth of the alumina. Moreover, $\text{ZrO}_2$ grains are homogenously distributed in the alumina matrix. SEM images confirm also the high densification of yttria stabilized zirconia samples.

Analyzing the values of Vickers hardness (Fig. 5) it can be concluded that all ZTA composites are characterized by higher hardness than $\text{ZrO}_2$, as expected. However, in case of $\text{Al}_2\text{O}_3$ samples the calculated value is lower than anticipated. It can be explained by the comparison of the microstructure of alumina and other samples (Fig. 4) where in case of alumina some mentioned above defects are visible.

In case of ZTA composites one of the most important parameter is fracture toughness. According to the literature and own experience the major difficulties in determining reliable fracture toughness values by Vickers indentation tests are: defining the type of formed cracks, precise measurements of the crack length and application of a suitable calculation model [33]. Depending on the mathematical model used in the calculations of fracture toughness, the reported values of $K_{IC}$ for Y-TZP (4.1 wt. % of yttria) varied from 3.96-6.40 MPam$^{0.5}$ [33]. It therefore shows that both the type of powder, samples preparation and model selection strongly influences the $K_{IC}$ which probably should not always be treated as absolute values.

The measurements of the mechanical properties of ZTA composites requires deepened studies [34,35], however in this paper the Authors concentrated just on basic properties which would allow to evaluate the usefulness of the new ACR-MAN monomer.

All ZTA samples were characterized by higher values of $K_{IC}$ than monophase alumina and zirconia samples. No significant differences have been observed taking into consideration the type
of monomer used. It means that the new monomer ACR-MAN is a good alternative for commercially available HEA, because it allows to obtain uniform and highly densified ceramic samples and additionally facilitates the shaping process by limiting the negative effect of oxygen inhibition.

4. Conclusions

The synthesis of the new monomer 3,4-di-acryloyl-D-mannitol (ACR-MAN) has been elaborated as the III stage process. The monomer is dedicated to gelcasting shaping method. ACR-MAN influences the rheological characteristics of ceramic suspensions by increasing the viscosity at low shear rates. Thus, it contributes to the limitation of the oxygen inhibition which is undesired phenomenon in gelcasting. The application of ACR-MAN allowed to obtain ZTA composites characterized by high relative density and uniform microstructure. Zirconia grains were homogenously distributed in alumina matrix. ZTA composites were characterized by higher fracture toughness than monolithic alumina and zirconia. The comparison of the calculated $K_{IC}$ values should be done taking into consideration the mathematical model selection, powder characteristics and samples preparation.

Acknowledgements

The project has been financially supported by National Science Centre of Poland (Agreement No. UMO-2014/15/D/ST5/02574).

REFERENCES

[1] A. Heel, P. Holtappels, T. Graule, On the synthesis and performance of flame-made nanoscale La$_{0.6}$Sr$_{0.4}$CoO$_{3+y}$ and influence on the application as an intermediate temperature solid oxide fuel cell cathode, J. Power Sources. 195, 6709-6718 (2010).


