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Raman Spectra Studies of Inner "Anode | electrolyte" Interface on ESC and ASC SOFCs

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In this work we present the results of *in-situ* case studies of fuel oxidation at the SOFC anode for anode-supported cells with thinfilm electrolyte deposited by magnetron sputtering technique in comparison with studies carried out on optically transparent singlecrystal membrane based electrolyte-supported model SOFC. Changes of the valence state of Ce ions were studied under different current loads applied to the cell, these changes were indicated in the Raman spectra obtained from inner interface of electrolyte membrane and anode electrode. Area of the corresponding peak in Raman spectra of ceria was studied for different working conditions for both cells constructions. Special processing technique gave opportunity to obtain more relevant data.

Introduction

Power plants based on solid oxide fuel cells (SOFCs) are among most promising power sources for the electrical and heat generation from fossil fuels (1-3). Electrode performance dramatically influences on SOFC efficiency (4-6). One needs to study the mechanisms and kinetics of the electrochemical processes at the electrodes to modify them in order to reduce the working temperature (7-8). Majority of techniques do not give this opportunity because of the intense heat radiation, geometrical factor (namely need in isolated gas chambers for fuel cell operation), high current loads in working conditions and aggressive gases presence as well. Raman spectroscopy is one of the perspective techniques to study electrochemical oxidation of the fuel at the anode electrode, as it is non-invasive, remote and molecular specific experimental approach. Raman spectroscopy is nowadays widely used to conduct the *in-situ* studies of operating SOFCs. The most important tasks solved by Raman spectroscopy in in-situ studies of SOFC are sulfur tolerance of anodes (9-12), mechanisms of fuel oxidation (13-21), carbon deposition (13,22-33), mechanical stresses (34-35), degradation of anodes in coarse of fuel cell operation (36-37), interaction between cathode and current collector (38). Ex-situ and in-situ studies of basic materials (start properties and aging) applied in SOFC manufacture are also commonly used by different research groups (39-47).

Majority of research groups are limited by outer boundaries of model cells because of low penetration depth of light and thus low depth of the point one can get the scattered signal from. Previously we described the special geometry (48) of the model samples based on optically transparent single-crystal solid electrolyte membranes as well as experimental device (49), which combines electrochemical and optical parts to create the excitation radiation and to collect the scattered one. Novel geometry and hightemperature Raman setup were used to study the anode processes on electrolytesupported SOFC with thick solid electrolyte for the cases of basic anode material – nickel oxide (50), open-circuit conditions (51) and under different current loads (52-53). The Raman spectra of ceria were found sensitive enough with respect to the variations of anodic current and fuel gas mixture composition, which induces cerium valence state changes in GDC.

One needs optically transparent solid electrolyte membrane to reach the inner interface between fuel electrode and anion conductor membrane in order to conduct the studies of the most electrochemically active zone instead of outer boundaries of the sample. One approach is application of optically transparent single-crystalline membrane. Another approach is use of thin-film membrane, as thick ceramic solid electrolyte has a lot of grain boundaries, which scatter the excitation radiation. Now we present results of the *in-situ* case studies of fuel oxidation at the SOFC anode for anode-supported cells with thin-film electrolyte deposited by magnetron sputtering technique in comparison with studies conducted on single-crystal membrane based electrolyte-supported model SOFC. Modified procedure of spectra processing give opportunity to obtain more relevant results for both electrolyte- and anode-supported cells.

Experimental

Experimental techniques

Microstructure of multilayered solid oxide fuel cells was studied by means of scanning election microscope (SEM) with a LEO Supra 50VP field emitting cathode. The device was equipped with an INCA Energy+ system of energy-dispersive X-ray microanalysis. SEM images were also obtained using Dual Beam VERSA 3D HighVac (FEI) setup.

Experimental setup for *in-situ* Raman studies combined with electrochemical investigations

Combined experimental setup for simultaneous studies by means of Raman spectroscopy and traditional electrochemical techniques (I-V curves, chronopotetiometry as well as impedance spectroscopy) was described elsewhere (48-49). This setup consists of two main parts: a block to create working conditions of operating fuel cells (temperature, fuel and oxidant gas mixtures, current load) and a block to create excitation radiation and to collect the scattered one.

Model samples

In this work we used two types of planar solid oxide fuel cells: electrolyte supported structures as it was done in previous works (49,51-53) and anode-supported model SOFC. Switch to anode supported ones gives opportunity to significantly reduce the fuel cell resistance and thus transit to lower operating temperatures and higher current loads. Construction of sublayers for both types of model cells is presented in figure 1.



Figure 1. Construction of model samples for electrolyte-supported (a) and anodesupported (b) structures.

<u>Electrolyte-supported model SOFCs</u>. Electrolyte-supported fuel cells were based on optically transparent solid electrolyte membranes manufactured by means of directed melt crystallization in cold crucible by research group in A.M. Prokhorov Institute of General Physics RAS (Russia) (54-55). Despite 10Sc1YSZ (89 mol% $ZrO_2 + 10 mol\%$ Sc₂O₃ + 1 mol% Y₂O₃) composition has the highest ionic conductivity in the family of cubic stabilized zirconia materials (56-58), we used 8YSZ (92 mol% $ZrO_2 + 8 mol\%$ Y₂O₃) material because it has more simple Raman spectra (59) and can be easily separated from the total spectra to receive the useful signal. Optically transparent electrolyte membranes were cut from the crystal, ground and polished, its thickness was controlled on a level of about 250 um.

Electrode deposition routine was optimized in previous work (60-62). Both electrodes were deposited via screen print technique using ceramic-organic screen print pastes by means of Ekra E2 (Germany) machine. GDC (90 mol% CeO₂ + 10 mol% Gd₂O₃) sub-layer was introduced in a construction of anode electrode, as this materials has lines in Raman spectra that are very sensitive to the oxygen stoichiometry in crystal lattice (63). Other two layers of anode electrode were based on NiO/GDC and NiO/10Sc1CeSZ composite materials. Anode electrode was fired in air at 1300°C for 2 hours.

Cathode was based on A-deficient LSM $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-d}$ material and consisted of LSM/10Sc1CeSZ (89 mol% ZrO₂ + 10 mol% Sc₂O₃ + 1 mol% CeO₂) composite. Cathode electrode was fired in air at 1100°C for 2 hours.

<u>Anode-supported model SOFCs</u>. This type of model cells was based on two-layered anode supports from SOFCMAN (China). Two thin-film electrolyte sublayers – GDC and YSZ – were deposited using magnetron sputtering technique in Institute of High-Current Electronics SB RAS (Russia). Cathode electrode – LSM/10Sc1CeSZ composite

- was deposited using same routine as for electrolyte-supported cells and fired according to the same high-temperature regime.

Platinum electrodes were used for the organization of current-collection from both types of experimental cells, they were fired in air at 900°C for 1 hour. Comparative SEM-images of cross-sections of electrolyte- (left) and anode-supported (right) cells are presented in figure 2.



Figure 2. SEM-images of cross-sections of electrolyte- (left) and anode-supported (right) model solid oxide fuel cells.

One can observe on figure 2 left a single-crystal membrane, which is situated in a bottom part of the image. Screen-printed indicative GDC layer has thickness of about 2-3 um. Functional anode sublayer is about 5 um thick, it has clear interface with GDC sublayer and consists of submicron particles. Current-collecting anode sublayer has a porosity with larger size (about micron), it has the same thickness of about 10 um.

Figure 2b shows SEM-image of cross section of anode-supported cell. Two-layered commercially available SOFCMAN support is located in upper part of the picture. Magnetron sputtered indicative GDC sublayer has close thickness to electrolyte-supported structure – about 2-3 um. Solid electrolyte membrane is rather dense and obviously gas-tight, in this case electrolyte has polycrystalline structure. Cathode electrode is porous, has clear interface with solid electrolyte membrane.

Results and discussion

Comparison of room temperature spectra

Difference between open circuit conditions spectra from inner interface of fuel electrode and solid electrolyte membrane for electrode- and anode-supported SOFCs is obvious even and especially at room temperature, when Ce has maximal oxidation state. Comparison of spectra is presented in figure 3.



Figure 3. Comparison of room temperature Raman spectra received from the inner interface of the anode electrode and solid electrolyte membrane for electrolyte- (left) and anode-supported (right) model solid oxide fuel cells.

An obvious difference is influence of parasitic sub-spectrum of YSZ membrane. It is quite significant for electrolyte-supported structure (left) and much lower for anode-supported one (right). All the peaks on both spectra can be attributed to Raman spectra of nickel oxide, zirconia and ceria. In previous studies (52-53), as in the current work, we analyze the oxygen pressure in the fuel chamber by studying the evolution of the line intensity with a shift of 460 cm⁻¹, which is sensitive to local oxygen stoichiometry in the crystal lattice. From the graphs in figure 3 left, it can be seen that for the case of samples with a supporting electrolyte, the intensity of the line of interest to us substantially exceeds the intensity of other lines in the spectrum, it is rather separated from other spectral lines. This feature allowed us in previous works to isolate the line of interest to us by simply subtracting the baseline, which was calculated as a third-degree polynomial, the derivative of which at the edges of the extracted peak coincides with the derivative of the Raman signal.

One can see on graph in figure 3 right that in case of anode-supported cells line of interest with a shift of 460 cm⁻¹ is comparable in intensity with neighboring lines, which does not allow us to repeat a simple signal processing procedure. In this case, a more complex procedure was used, described in detail in the next subsection. This procedure gave an opportunity to receive more relevant data for anode-supported cells as well as for electrolyte-supported structures.

Processing of spectra for cases of electrolyte- and anode-supported cells

In the process of obtaining Raman spectra from the "electrolyte | anode" interface under the conditions of the fuel cell operation, many difficulties complicate the analysis of the obtained data: low intensity of the useful signal, the effect of radiation from the heated body, the influence of the frequency-temperature factor, the complex shape of the spectrum. In this connection, the following methodology was developed for conducting an experiment, as well as processing the Raman spectra. Procedure of spectra processing consisted of several computation steps. First step of this routine is presented in figure 4.



Figure 4. Comparison of first step in Raman spectra processing routine – collection of spectra for 100 second. Insert – initial spectrum before collection. Left – electrolyte-supported cell, right – anode-supported cell.

Due to the relatively high operating temperature of SOFC, the intensity of heat radiation becomes much higher than the signal under study. To improve the measurement statistics, a cyclic accumulation of the signal (100 seconds) and the subtraction of the heated body radiation spectrum at each cycle are performed (figure 4). The inset in figure 4 shows a single spectrum before accumulation, it has quite intense noise, which makes the analysis particularly impossible.

One can observe an obvious difference between the data obtained using electrolyteand anode-supported cells. The main difference is role of our line of interest (460 cm⁻¹) in comparison to other lines – this role is significantly higher for anode-supported structures (right image in figure 4). As for electrolyte-supported cells, a more significant role is played by zirconia line.

The second step in processing routine is showed in figure 5.



Figure 5. Fuel mixture composition influence on 460 cm^{-1} region of Raman spectrum after frequency-temperature correction and normalization on integral. Inset – full-range Raman spectra after frequency-temperature correction and normalization on integral of the spectrum. Left – electrolyte-supported cell, right – anode-supported cell.

The occupation number of the vibrational levels near the line of exciting radiation strongly depends on the temperature. In this connection, the correction of the obtained data to the temperature-frequency factor is required (64-65). This normalization is carried out in accordance with the Bose-Einstein statistics, to which the phonons of the crystal lattice responsible for Raman scattering obey. To bring the spectra to a similar form for their further comparison, we normalized the integral under the curve (inset on figure 5). Dependence of Raman spectra processed in this way on fuel mixture is presented in main part of figure 5. One can easily observe a strong dependence of the intensity of spectral line with Raman shift of 460 cm⁻¹ on hydrogen partial pressure. Addition of hydrogen to the mixture leads to reduction of spectral line as we decrease the amount of oxygen in outer gas as well as in GDC crystal structure, it leads to decrease of Raman scattering probability.

It is once again worth noticing, that there is an obvious difference between Raman spectra collected and processed using electrolyte- and anode-supported samples. The relative intensity of 460 cm⁻¹ spectra line is rather high for the case of anode-supported model SOFCs (figure 5 right). As for electrolyte-supported cells (figure 6 left), the major intensity is presented by zirconia line, which is not the studied one and it will be decomposed from the spectra as parasitic one in following steps.

Consequent step of signal processing is decomposition of the spectrum into different lines as it consists of sub-spectra attributed to different fuel cell materials. Decomposition procedure is shown in figure 6.



Figure 6. Decomposition of Raman spectrum for: left – electrolyte-supported cell, right – anode-supported cell.

One can observe from figure 6, that Raman spectrum obtained was decomposed into separate spectra lines using Gauss fit presentation of zirconia peaks and ceria peak of interested (460 cm⁻¹, blue line). Zirconia peaks were fitted by Gauss curves with the centers at Raman shifts in the ranges near to values of 260 (orange line), 355 (violet), 540 (green) and 600 cm⁻¹ (red). It is obvious, that resulting cumulative fit spectrum (yellow dotted line) fits the experimental data (black line) in an excellent way.

Our spectra line of interest (460 cm⁻¹) is once again the most intense in a spectrum for anode-supported structures (right image). It is also quite noticeable for the spectrum of electrolyte-supported cells (left picture), but not the most intense one.

Result of the processing routine described above is separate spectral line with Raman shift of 460 cm⁻¹ and its dependence on fuel composition (partial pressure of hydrogen in its humidified mixture with nitrogen). This result is presented in figure 7.



Figure 7. Dependence of decomposed spectral line with Raman shift of 460 cm^{-1} on fuel mixture composition. Left – electrolyte-supported cell, right – anode-supported cell.

One can once again notice a significant dependence of this spectral line intensity on partial pressure of hydrogen in fuel mixture. Addition of hydrogen to this mixture leads to decrease of line intensity. This result can be explained by reduction of oxygen amount in GDC crystal latice as atmosphere becomes more reducing one. Decrease of oxygen amount leads to decrease of probability of Raman scattering and thus to the decrease of corresponding line intensity. In the results presented in following parts of this manuscript we used integral area of this peak instead of simple intensity in maximum as this area is proportional to probability of Raman scattering and more informative from the point of view of physical reasons.

Comparison of results obtained using electrolyte- and anode-supported cells

Area of the peak with Raman shift of 460 cm⁻¹ was estimated for two types of cells (electrolyte- and anode-supported) for different fuel compositions. Mixture of hydrogen and nitrogen was used in all the experiments: $H_2/N_2=50/50$ and 10/90 for electrolyte-supported cells and 50/50 and 100/0 for anode-supported solid oxide fuel cells. Results of these studies are presented in figure 8. Peak area was normalized on the line intensity for the case of $H_2/N_2=1/1$ fuel mixture and open circuit conditions.



Figure 8. Peak area for the line with Raman shift of 460 cm^{-1} for different types of cell (electrolyte supported – black, anode supported – red) and fuel compositions (under different current loads).

One can observe from figure 8, that transition to anode-supported structures give opportunity to significantly extend the range of current loads available. Maximal current load applied is more then 2 times higher for the case of anodic support. The general view of the dependence is quite similar for both cell types, it can be attributed to the transport of oxygen anions (O^{2-}) from solid electrolyte membrane to anode electrode.

Conclusions

In present work we conducted comparative *in-situ* studies of planar electrolyte- and anode-supported model solid oxide fuel cells by means of combined technique which gives opportunity to do simultaneous investigations via Raman spectroscopy and electrochemical techniques. Introduction of anode-supported cells led to significant reduction of working temperature and extension of current load range. Comparative studies gave opportunity to find limitations of both geometries. Special processing technique was developed and applied to spectra obtained using both constructions of SOFC samples.

Dependences of Raman spectral line at 460 cm^{-1} on current load applied were obtained for both types of cells and for different compositions of fuel mixture. It was shown, that transition to anode-supported structures with ceramic thin-film electrolyte gives opportunity to get spectroscopic information from region of inner "electrolyte | anode" interface. Moreover Raman measurements on ASC samples show rather higher sensitivity and allow to extend the range of current loads (up to 2 A/cm²) and working temperatures (650-750°C). General view of dependences is rather close, it can be attributed to transport of oxygen anion from solid electrolyte membrane to anode electrode.

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References

- 1. M. Shamoushaki, M. A. Ehyaei, F. Ghanatir, *Energy*, 134, 515 (2017).
- 2. A. Perna, M. Minutillo, E. Jannelli, V. Cigolotti, S. Woo Nam, K. Joong Yoon, *Appl. Energy*, **227**, 80 (2018).
- 3. F. Ramadhani, M. A. Hussain, H. Mokhlis, S. Hajimolana, *Renev. Sust. Energ. Rev.*, **76**, 460 (2017).
- P. A. Connor, X. Yue, C. D. Savaniu, R. Price, G. Triantafyllou. M. Cassidy, G. Kerherve, D. J. Payne, R. C. Maher, L. F. Cohen, R. I. Tomov, B. A. Glowacki, R. V. Kumar, J. T. S. Irvine, *Adv. Energy Mater.*, 8(23), 1800120 (2018).
- 5. J. A. Cebollero, R. Lahoz. M. A. Laguna-Bercero, A. Larrea, J. Power Sources, **360**, 336 (2017).
- 6. D. Papurello, C. Iafrate, A. Lanzini, M. Santarelli, Appl. Energ., 208, 637 (2017).
- 7. E. D. Wachsman, K. T. Lee, *Science*, **334**(6058), 935 (2011).

- 8. H. Gu, H. Chen, L. Gao, Y. Zheng, X. Zhu, L. Guo, *Int. J. Hydrog. Energ.*, **34**(5), 2416 (2009).
- 9. Z. Cheng, M. Liu, Solid State Ionics, 178(13-14), 925 (2007).
- 10. Z. Cheng, J.-H. Wang, Y.M. Choi, L. Yang, M.C. Lin, M. Liu, *Energ. & Environment. Sci.*, 4, 4380 (2011).
- 11. H. H. Thi, B. Saubat, N. Sergent, T. Pagnier, Solid State Ionics, 272, 84 (2015).
- 12. Z. Cheng, H. Abernathy, M. Liu, J. Phys. Chem. C, 111(49), 17997 (2007).
- 13. M. B. Pomfret, J. Marda, G. S. Jackson, B. W. Eichhorn, A. M. Dean, R. A. Walker, J. Phys. Chem. C, 112(13), 5232 (2008).
- 14. M. B. Pomfret, J. C. Owrutsky, R. A. Walker, Anal. Chem., 79(6), 2367 (2007).
- 15. B. C. Eigenbrodt, M. B. Pomfret, D. A. Steinhurst, J. C. Owrutsky, R. A. Walker, *J. Phys. Chem. C*, **115**(6), 2895 (2011).
- 16. M. B. Pomfret, J. Owrutsky, R. Walker, ECS Trans., 11(27), 99 (2008).
- 17. J. D. Kirtley, D. A. Steinhurst, J. C. Owrutsky, M. B. Pomfret, R. A. Walker, *Phys. Chem. Chem. Phys.*, 16, 227 (2014).
- 18. J. D. Kirtley, M. B. Pomfret, D. A. Steinhurst, J. C. Owrutsky, R. A. Walker, J. *Phys. Chem. C*, **119**(23), 12781 (2016).
- 19. B. Eigenbrodt, J. Kirtley, R.A. Walker, ECS Trans., 35(1), 2789 (2011).
- 20. M. B. Pomfret, R. A. Walker, J. C. Owrutsky, J. Phys. Chem. Lett., 3(20), 3053 (2012).
- 21. L. Yang, Y. M. Choi, W. Qin, H. Chen, K. Blinn, M. Liu, P. Liu, J. Bai, T. A. Tyson, M. Liu, *Nat. Comm.*, **2**, 357 (2911).
- 22. K. S. Blinn, H. Abernathy, X. Li, M. Liu, L. A. Bottomley, M. Liu, *Energ. & Environment. Sci.*, **5**, 7913 (2012).
- 23. J. Kirtley, A. Singh, D. Halat, T. Oswell, J. M. Hill, R. A. Walker, *J. Phys. Chem. C*, **117**(49), 25908 (2013).
- 24. X. Li, M. Liu, S.Y. Lai, D. Ding, M. Gong, J.-P. Lee, K. S. Blinn, Y. Bu, Z. Wang, L. A. Bottomley, F. M. Alamgir, M. Liu, *Chem. Mater.*, **27**(3), 822 (2016).
- 25. W. Li, Y. Shi, Y. Luo, Y. Wang, N. Cai, J. Power Sources, 276. 26 (2015).
- 26. X. Li, M. Liu, J.-P. Lee, D. Ding, L. A. Bottomley, S. Park, M. Liu, *Phys. Chem. Chem. Phys.*, **17**, 21112 (2015).
- 27. M. D. McIntyre, D. M. Neuburger, R. A. Walker, ECS Trans., 66(32), 11 (2015).
- 28. V. Duboviks, R. C. Maher, M. Kishimoto, L. F. Cohen, N. P. Brandon, G. J. Offer, *Phys. Chem. Chem. Phys.*, **16**, 13063 (2014).
- 29. R. C. Maher, V. Duboviks, G. J. Offer, M. Kishimoto, N. P. Brandon, L. F. Cohen, *Fuel Cells*, **13**(4), 45 (2013).
- K. W. Reeping, D. M. Halat, J. D. Kirtley, M. D. McIntyre, R. A. Walker, *ECS Trans.*, 61(1), 57 (2014).
- 31. K. Yashiro, M. Takase, K. Sato, T. Kawada, J. Mizusaki, *ECS Trans.*, **16**(51), 213 (2009).
- K. Yashiro, K. Takeda, T. Taura, T. Otake, A. Kaimai, Y. Nigara, T. Kawada, J. Mizusaki, Proc. Eletrochem. Soc., PV2003-07, 714 (2003).
- 33. F. Chen, S. Zha, J. Dong, M. Liu, Solid State Ionics, 166, 269 (2004).
- 34. M. Nagai, F. Iguchi, S. Onodera, N. Sata, T. Kawada, H. Yugami, *ECS Trans.*, **35**(1), 519 (2011).
- 35. J. Van herle, R. Ihringer, N. M. Sammes, G. Tompsett, K. Kendall, K. Yamada, C. Wen, T. Kawada, M. Ihara, J. Mizusak, *Solid State Ionics*, **132**, 333 (2000).
- 36. J. D. Kirtley, M. D. McIntyre, D. M. Halat, R. A. Walker, *ECS Trans.*, **50**(44), 3 (2013).

- 37. E. J. Brightman, R. Maher, D. G. Ivey, G. Offer, N. P. Brandon, *ECS Trans.*, **35**(1), 1407 (2011).
- 38. H. W. Abernathy, E. Koep, C. Compson, Z. Cheng, M. Liu, J. Phys. Chem. C, **112**(34), 13299 (2008).
- 39. Z.-Y. Pu, J.-Q. Lu, M.-F. Luo, Y.-L. Xie, J. Phys. Chem. C., 111(50), 18695 (2007).
- 40. A. Grimaud, J.M. Bassat, F. Mauvy, P. Simon, A. Canizares, B. Rousseau, M. Marrony, J. C. Grenier, *Solid State Ionics*, **191**(1), 24 (2011).
- 41. R. C. Maher, L. F. Cohen, P. Lohsoontorn, D. J. L. Brett, N. P. Brandon, *J. Phys. Chem. A*, **112**(7), 1497 (2008).
- 42. M. Guo, J. Lu, Y. Wu, Y. Wang, M. Luo, Langmuir, 27(7), 3872 (2011).
- 43. A. Mineshige, T. Taji, Y. Muroi, M. Kobune, S. Fujii, N. Nishi, M. Inaba, Z. Ogumi, *Solid State Ionics*, **135**(1-4), 481 (2000).
- 44. K. Nomura , Y. Mizutani , M. Kawai , Y. Nakamura , O. Yamamoto, *Solid State Ionics*, **135** 235 (2000).
- 45. M. Hattori, Y. Takeda, Y. Sakaki, A. Nakanishi, S. Ohara, K. Mukai, J.-H. Lee. T. Fukui, *J. Power Sources*, **126**(1-2), 23 (2004).
- 46. J.-W. Lee, Z. Liu., L. Yang, H. Abernathy, S.-H. Choi, H.-E. Kim, M. Liu, J. *Power Sources*, **190**(2), 307 (2009).
- 47. N. Mironova-Ulmane, A. Kuzmin, I. Steins, J. Grabis, I. Sildos, M. Pärs, J. Phys.: Conf. Ser., 93 12039 (2007).
- 48. D. A. Agarkov, I. N. Burmistrov, F. M. Tsybrov, I. I. Tartakovskii, V. V. Kharton, S. I. Bredikhin, V. V. Kveder, *ECS Trans.*, **68**(1), 2093 (2015).
- 49. D. A. Agarkov, I. N. Burmistrov, F. M. Tsybrov, I. I. Tartakovskii, V. V. Kharton, S. I. Bredikhin, *Russ. J. Electrochem.*, **52**(7), 600 (2016).
- 50. I. N. Burmistrov, D. A. Agarkov, I. I. Tartakovskii, V. V. Kharton, S. I. Bredikhin, *ECS Trans.*, **68**(1), 1265 (2015).
- 51. D. A. Agarkov, I. N. Burmistrov, F. M. Tsybrov, I. I. Tartakovskii, V. V. Kharton, S. I. Bredikhin, *Solid State Ionics*, **302**, 133 (2017).
- 52. D. A. Agarkov, I. N. Burmistrov, F. M. Tsybrov, I. I. Tartakovskii, V. V. Kharton, S. I. Bredikhin, *Solid State Ionics*, **319C**, 125 (2018).
- 53. С. И. Бредихин, Д. А. Агарков, А. С. Аронин, И. Н. Бурмистров, Д. В. Матвеев, Ф. М. Цыбров, В. В. Хартон, АЭЭ, **4-6**, 70 (2018).
- 54. M. A. Borik, E. E. Lomonova, V. V. Osiko, V. A. Panov, O. E. Porodnikov, M. A. Vishnyakova, Yu. K. Voron'ko, V. V. Voronov, J. Cryst. Growth, 275, e2173 (2005).
- 55. V. I. Aleksandrov, V. V. Osiko, A. M. Prokhorov and V. M. Tatarintsev, *Russ. Chem. Rev.*, **47** (3), 213 (1978).
- 56. D. A. Agarkov, M. A. Borik, S. I. Bredikhin, A. V. Kulebyakin, I. E. Kuritsyna, E. E. Lomonova, F. O. Milovich, V. A. Myzina, V. V. Osiko, E. A. Agarkova, N. Yu. Tabachkova, *Russ. J. Electrochem.*, **54**(6), 459 (2018).
- 57. I. E. Kuritsyna, S. I. Bredikhin, D. A. Agarkov, M. A. Borik, A. V. Kulebyakin, F. O. Milovich, E. E. Lomonova, V. A. Myzina, N. Yu. Tabachkova, *Russ. J. Electrochem.*, 54(6), 481 (2018).
- 58. D. A. Agarkov, M. A. Borik, V. T. Bublik, S. I. Bredikhin, A. S. Chislov, A. V. Kulebyakin, I. E. Kuritsyna, E. E. Lomonova, F. O. Milovich, V. A. Myzina, V. V. Osiko, N.Yu. Tabachkova, *Solid State Ionics*, **322**, 24 (2018)
- 59. W. Araki, T. Koshikawa, A. Yamaji, T. Adachi, *Solid State Ionics*, **180**(28-31) 1484 (2009).

- 60. I. Burmistrov, D. Agarkov, S. Bredikhin, Yu. Nepochatov, O. Tiunova, O. Zadorozhnaya, *ECS Trans.*, **57**(1), 917 (2013).
- 61. I. N. Burmistrov, D. A. Agarkov, F. M. Tsybrov, S. I. Bredikhin, *Russ. J. Electrochem.*, **52**(7), 669 (2016).
- 62. I. N. Burmistrov, D. A. Agarkov, E. V. Korovkin, D. V. Yalovenko, S. I. Bredikhin, *Russ. J. Electrochem.*, **53**(8), 873 (2017).
- 63. J. R. McBride, K. C. Hass, B. D. Poindexter, W. H. Weber, J. Appl. Phys., 76, 2435 (1995).
- 64. P. F. McMillan, G. H. Wolf, Rev. Mineral., 32, 247 (1995).
- 65. D. A. Long, D.A., Raman spectroscopy, McGraw-Hill, New York, p. 276 (1977).