TARGET COMPREHENSIVE PROGRAM SCIENTIFIC RESEARCH NAS of UKRAINE

Development of scientific principles of obtaining, storage and use of hydrogen in autonomous energy supply systems

Structural, impedance and electron microscopic studies of multilayer systems for low-temperature (600 ° C) fuel cell, project № 17

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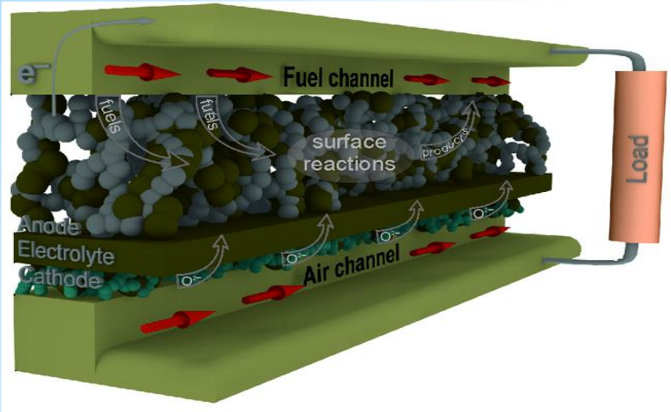


Fuel cell scheme

The creation of ceramic oxide fuel cells based on multilayer systems due to high efficiency, compactness and environmental friendliness is promising. The use of electrolyte, which has a high conductivity in oxygen, reduces ohmic losses, which can significantly increase the specific power of oxide fuel cells. Therefore, as a solid electrolyte, it is promising to use a zirconium matrix ZrO2, stabilized by complex oxides of scandium (III) and cerium (IV), which are characterized by high oxygen conductivity. At the same time, the method of synthesis of powders of stabilized zirconium dioxide affects the electrophysical properties of the prepared electrolyte.

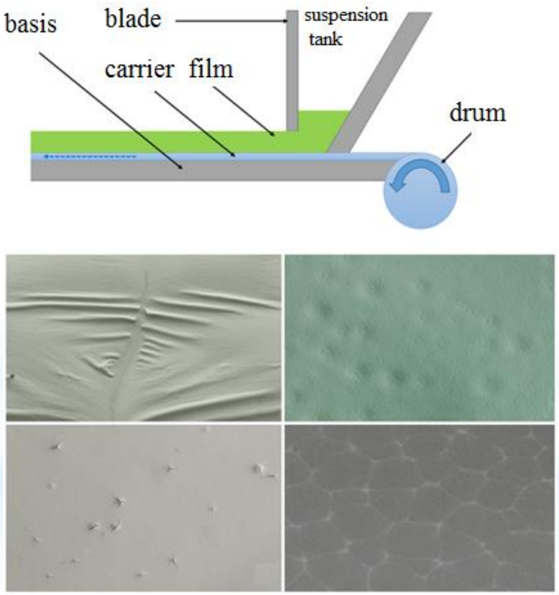
THE GOAL OF THE WORK

Development of preparation technology and structural, impedance and electron microscopic studies of multilayer systems based on thick films for low-temperature (600°C) fuel cell.

1. Synthesis and study of thick films $ZrO_2–Sc_2O_3–CeO_2$ i ZrO_2-Y_2O_3

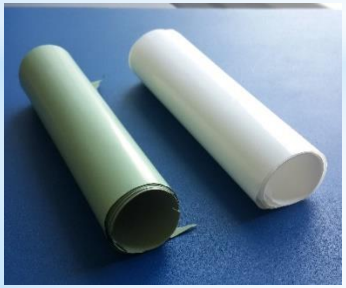
Thick films of electrolyte $ZrO_2 – Sc_2O_3 – CeO_2$ and ZrO_2-Y_2O_3 were prepared by tape casting of a suspension comprising organic (polyvinyl butyral, polyphthalate) and inorganic (weakly agglomerated nanopowders of appropriate compositions). The thick films were applied on a polymeric substrate with a hydrophobic layer, which allowed to cut loose the films after evaporation of solvents. The Film Applicator and Drying Time Recorder COATMASTER 510 equipped with a special knife was used for casting thick electrolyte films. Ultra-fast heating (thermal shock) from 20 to 500°C with subsequent slow (1°C / min) heating to the final synthesis temperature of 1200 - 1300°C allowed to significantly increase the density of thick films.

Device for films deposition



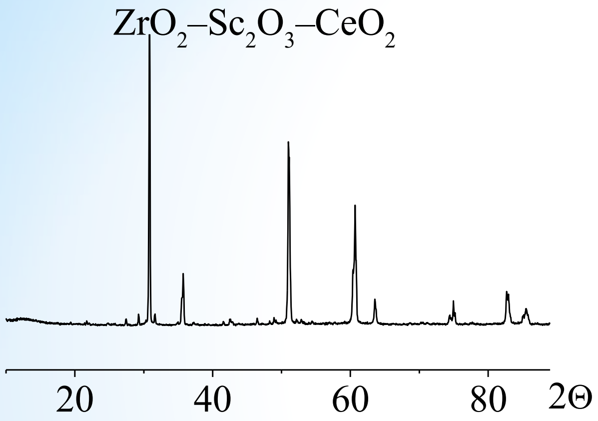
The scheme and microstructure of thick films prepared by the method of tape casting

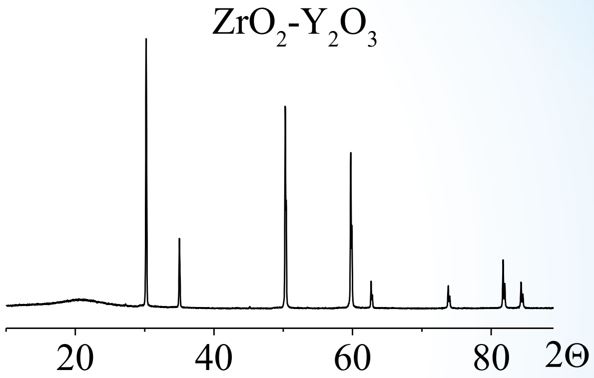
Films of different thickness:
80 μm, 160 μm and 320 μm
(from left to right)



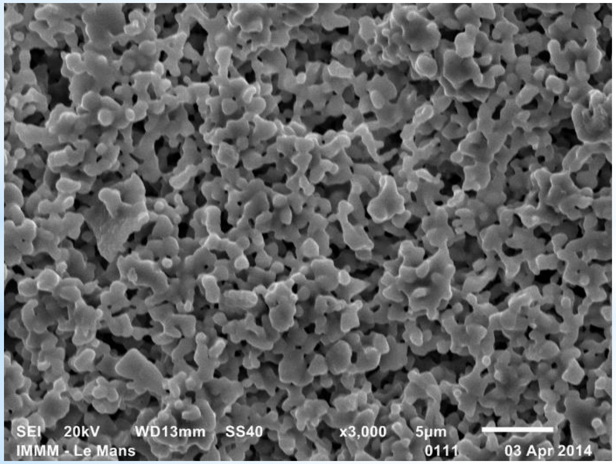
Tapes of thick anode and electrolyte films

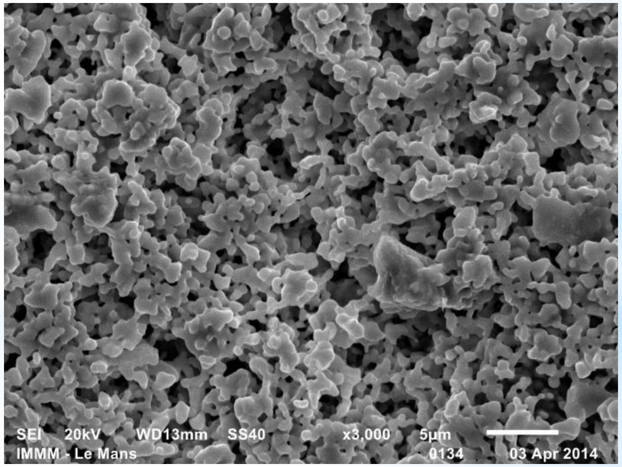
X-ray phase analysis showed that the prepared thick films are single-phase





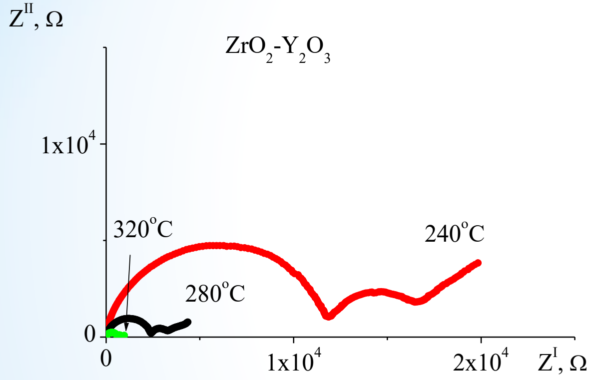
XRD patterns of thick electrolyte films

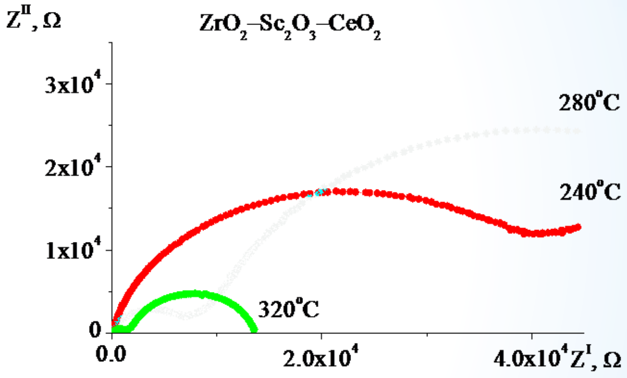




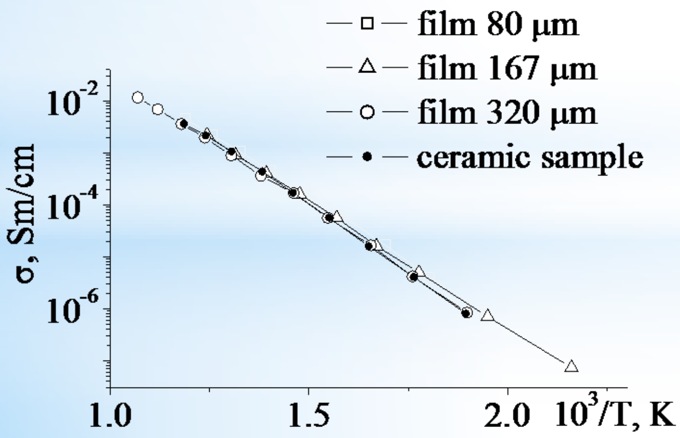
Surface microstructure of thick electrolyte films

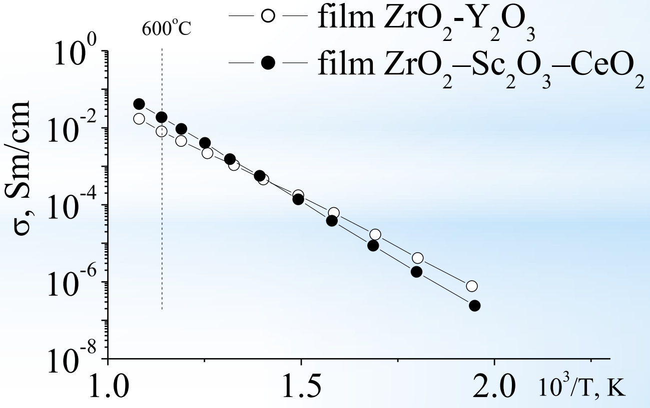
Complex impedance investigations of thick films in a wide frequency (1 Hz - 32 MHz) and temperature (20-700°C) ranges showed that the films of the composition ZrO_2 – Sc_2O_3 – CeO_2 are characterized by high oxygen conductivity, namely:
$1.8 \cdot 10^{-2}$ Sm/cm (at 600°C); $9 \cdot 10^{-2}$ Sm/cm (at 700°C)





Complex impedance curves in Nyquist coordinates of thick films at different temperatures





Temperature dependence of film conductivity

2. SYNTHESIS OF STABILIZED ZIRCONIUM DIOXIDE POWDER BY DEPOSITION FROM SOLUTIONS

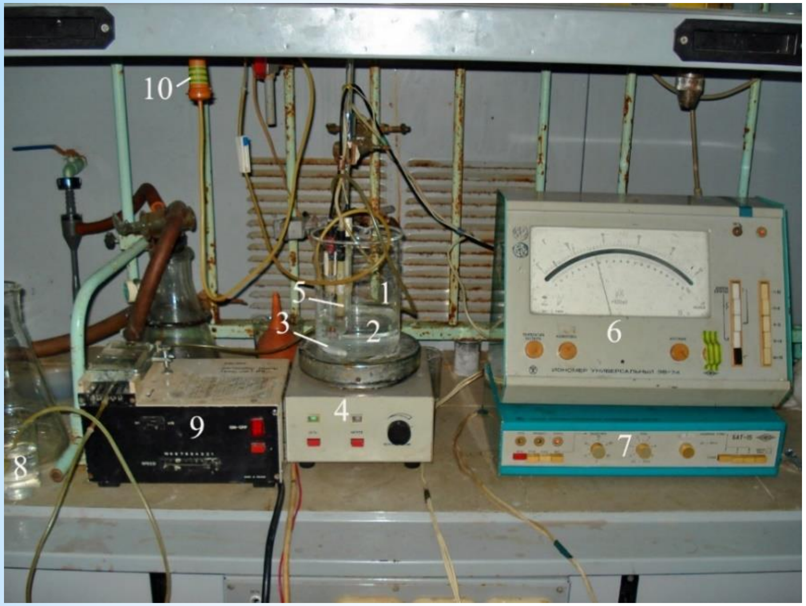


Photo of the installation for deposition

1 - glass reactor; 2 - mother liquor 3 - anchor of the magnetic bag; 4 - magnetic stirrer; 5 - pH-meter electrodes; 6 - pH meter; 7 - automatic titration unit (BAT); 8 - glass with a solution for precipitation; 9 - mechanical pump; 10 - solenoid valve BAT to block the supply of precipitator to the reactor.

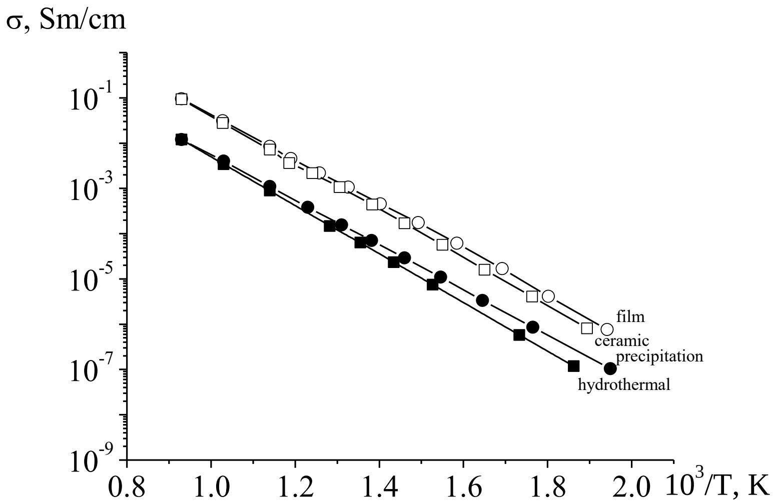
Nanopowders ZrO_2-Sc_2O_3-CeO_2 were synthesized by precipitation from aqueous solutions. $ZrCl_4$, $Sc(NO_3)_3$, $Ce(NO_3)_3$ and NH_4OH were used as starting reagents. It is established that when using sequential deposition at optimal pH values, weakly agglomerated nanopowders (Kfiltp = (0.8 ÷ 1.5) · 10^{-5} cm/s) are formed, which are easily washed, in contrast to sediments of the same composition, which are obtained by co-deposition (Kiltr = (2 ÷ 5)·(10^{-7} cm/s).

2. SYNTHESIS OF STABILIZED ZIRCONIUM DIOXIDE POWDER BY DEPOSITION FROM SOLUTIONS

High pressure reactor for synthesis of powders by hydrothermal method

The synthesis of the ZrO_2-Sc_2O_3-CeO_2 system was also performed by the hydrothermal method. The autoclave was heated to 250°C for holding time 24 hours at pressure 20MPa. The starting reagents were used as in the method of precipitation from solutions. Ceramic samples were obtained from hydrothermal powders. Sintering at temperatures of 1390-1400°C / 10-12 h resulted in single-phase ceramics with a cubic structure of zirconium dioxide. Impedance studies of ceramic samples in a wide frequency (1 Hz - 32 MHz) and temperature (20-800°C) ranges showed that the ceramics of the composition ZrO_2-Sc_2O_3-CeO_2 has the oxygen conductivity with the following characteristics: $9 \cdot 10^{-4}$ Sm/cm (at 600°C); $3.4 \cdot 10^{-3}$ Sm/cm (at 700°C); $1.2 \cdot 10^{-2}$ Sm/cm (at 800°C) activation energy - 1.07 eV, while the electron conductivity is 2 orders of magnitude lower compared to the conductivity of oxygen.

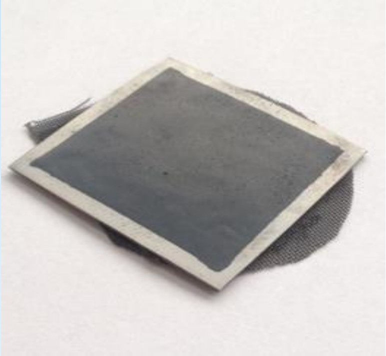
COMPARISON OF ELECTROPHYSICAL PROPERTIES OF STABILIZED ZIRCONIUM DIOXIDE PREPARED BY HYDROTHERMAL METHOD AND DEPOSITION FROM SOLUTIONS



Temperature dependence of specific conductivity of ceramics prepared by different methods.

Method of preparation	Activation energy, эВ	conductivity at 600°C, Sm/cm	conductivity at 700°C, Sm/cm	conductivity at 800°C, Sm/cm
hydrothermal	1.07	$9 \cdot 10^{-4}$	$3.4 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$
precipitation	1.015	$1.1 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$
film ZrO_2-Y_2O_3 -167 μm	1.03	$8.5 \cdot 10^{-3}$	$3.1 \cdot 10^{-2}$	$9.5 \cdot 10^{-2}$
Ceramic ZrO_2-Y_2O_3 -800 μm	0.98	$5.2 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$	$9.3 \cdot 10^{-2}$

A comparative study of the electrical properties of the developed fuel cell and a commercial analogue



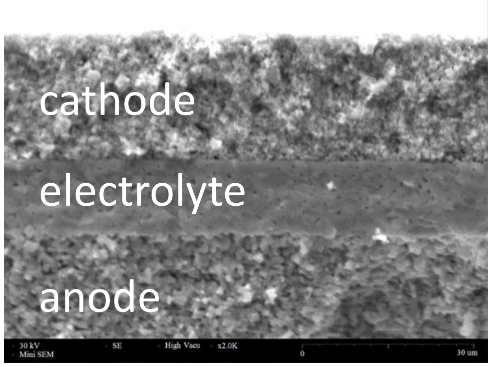
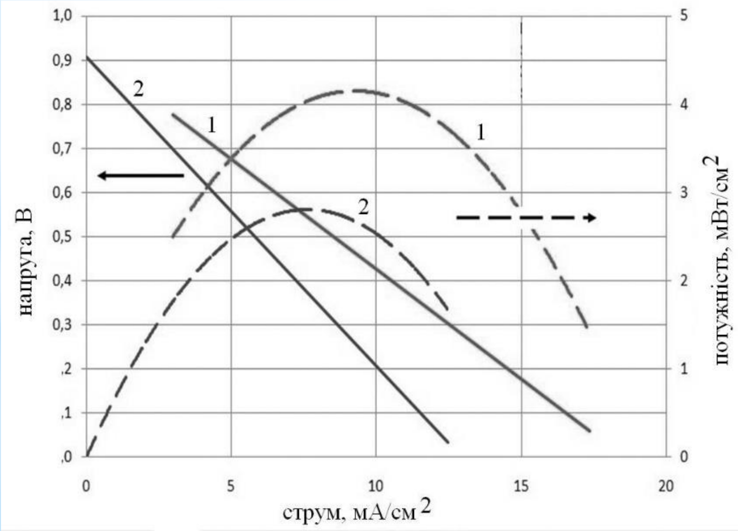


Photo and photomicrograph of a fuel cell made by tape casting; photo of the universal stand for testing fuel cells Scribner Teledyne Medusa RD 890CL



The made PDA has higher characteristics of efficiency of work in comparison with its commercial analog. Thus, when supplied with model fuel gas, the Ukrainian PDA demonstrated the maximum specific power at the level of 4.2 mW/cm^2 at 800^{o}C, while the commercial one - only 2.8 mW/cm^2.

Comparison of the electrical properties of the prepared fuel cell (1) with a commercial analogue (2); devices were tested under the same conditions.

CONCLUSIONS

1. The synthesis of $ZrO_2 – Sc_2O_3 – CeO_2$ and ZrO_2-Y_2O_3 was carried out, the structural and electrophysical features of thick films of these system were studied. It is established that thick films of $ZrO_2 – Sc_2O_3 – CeO_2$ composition are characterized by high oxygen conductivity, namely: $1.8 \cdot 10^{-2}$ cm / cm (at 600ºC); $9 \cdot 10^{-2}$ cm / cm (at 700ºC). It is established that only by using a combination of two different methods: type casting and lamination with subsequent heat treatment, it is possible to obtain multilayer, dense, thick films of ceramic electrolyte. The resulting multilayer system can be used as a model object in the manufacture of a stand of low-temperature (600ºC) film fuel cell.
2. Structural, impedance and electron microscopic studies of ceramic materials based on powders of the $(ZrO_2)_{0.80} (Y_2O_3)_{0.02} (Ce_2O_3)_{0.08}$ (8Ce2YSZ) system obtained by the deposition method were performed. It is established that ceramics of composition 8Ce2YSZ are characterized by high conductivity on oxygen, namely: $1.1 \cdot 10^{-3}$ Cm / cm (at 600ºC); $4 \cdot 10^{-3}$ cm / cm (at 700 ºC); $1.2 \cdot 10^{-2}$ Cm / cm (at 800 ºC) activation energy - 1.015 eV, while the electronic conductivity is lower by two orders of magnitude.
3. Structural, impedance and electron microscopic studies of ceramic materials based on powders of the $(ZrO_2)_{0.80} (Y_2O_3)_{0.02} (Ce_2O_3)_{0.08}$ (8Ce2YSZ) system obtained by the hydrothermal method were performed. It is established that the ceramics of the composition 8Ce2YSZ has the characteristics of high oxygen conductivity, namely: $9 \cdot 10^{-4}$ cm / cm (at 600ºC); $3.4 \cdot 10^{-3}$ cm / cm (at 700 ºC); $1.2 \cdot 10^{-2}$ Cm / cm (at 800 ºC) activation energy - 1.07 eV, while the electron conductivity is 2 orders of magnitude lower compared to the conductivity of oxygen.
4. It was found that the synthesized powders by different methods (hydrothermal method and precipitation method) based on zirconium dioxide stabilized by complex stabilizing additives are characterized in the temperature range (600-700ºC) by high ionic conductivity and can be used as solid electrolytes for low-temperature fuels.

LIST OF PUBLISHED WORKS OF THE PROJECT № 17

1. Y. Brodnikovskyi, N. McDonald, I. Polishko, D. Brodnikovskyi, I. Brodnikovska, M. Brychevskyi, L. Kovalenko, O. Vasylyev, A. Belous, R. Steinberger-Wilckens. Properties of 10Sc1CeSZ-3.5YSZ(33-, 40-, 50-wt.%) Composite Ceramics for SOFC Application Materials. *Today: Proceedings,* 2019, vol. 6, pp. 26–35

   DOI: 10.1016/j.matpr.2018.10.071
2. I. Polishko, S. Ivanchenko, R. Horda, Y. Brodnikovskyi, N. Lysunenko, L. Kovalenko. Tape casted SOFC based on Ukrainian 8YSZ powder. *Today: Proceedings*, 2019, vol. 6, pp. 237-241

   DOI: 10.1016/j.matpr.2018.10.100
3. Y. M. Ostroverkh, I. O. Polishko, D. M. Brodnikovskyi, L. L. Kovalenko, A. V. Samelyuk, O. D. Vasylyev, A. S. Ostroverkh. Mechanical behavior and electrical conductivity of zinc-oxideceramics. *Uspikhi materialoznavstva*, 2020, № 1, c. 46-54

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4. Rusetskii, L. L. Kovalenko, I. A. Slobodyanyuk, M. O. Danilov, S. S. Fomanyuk, V. O. Smilyk, A. G. Belous, G.Ya. Kolbasov. Photoelectrochemical systems for hydrogen evolution using ion-conducting membranes. *ECS Trans*, 2020, vol. 99(1), pp. 221-230

   DOI: 10.1149/09901.0221ecst
5. M.A. Gumenna, N.S. Klimenko, A.V. Stryutsky, L.L. Kovalenko, V.V. Kravchenko, A.V. Shevchuk, V.V. Shevchenko. Polymeric proton exchange media with ionic bonds in the main chain of the polymer. *Dopov. Nac. akad. nauk Ukr.* 2020, N12, pp. 60-66.

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6. А.О. Новохатська, Г.Я. Єкимов, Л.Л. Коваленко. Особливості структури і електропровідності катоду на основі манганіту неодима, обумовлені надлишковим марганцем. // XX ювілейна міжнародна науково-практична конференція «відновлювальна енергетика та енергоефективність у XXI столітті" 15-16 травня 2019 р. Київ.
7. Novokhatska, G. Akimov, L. Kovalenko. The study of ceramic composites based on zirconia and manganite with excess manganese for cathode of SOFCs // The 13th Conference for Young Scientists in Ceramics Department of Materials Engineering, Faculty of Technology Novi Sad, University of Novi Sad October 16-19, 2019.

8. В’юнов О.І., Коваленко Л.Л., Янчевський О. З., Білоус А.Г., Полішко І.О., Бродніковський Є.М., Іванченко С.Е., Лисуненко Н.О., Бродніковський Д.М., Бродніковська І.В., Барановський Д.І., Бричевський М.М., Васильєв О.Д. Проведення структурних, імпедансних та електронномікроскопічних досліджень багатошарових систем керамічного електроліту. // Наукова звітна сесія. 11 грудня 2019 р. с.27
9. Бродніковський Є.М., Полішко І.О., Лисуненко Н.О., Іванченко С.Е., Бродніковський Д.М., Чедрик В.І., Бродніковська І.В., Барановський Д.І., В’юнов О.І., Коваленко Л.Л., Янчевський О. З., Васильєв О.Д., Рагуля А.В., Білоус А.Г. Відпрацювання режимів виготовлення керамічної паливної комірки методом стрічкового лиття. // Наукова звітна сесія. 11 грудня 2019 р. с.28
10. В’юнов О.І., Коваленко Л.Л., Янчевський О. З., Білоус А.Г., Полішко І.О., Бродніковський Є.М., Лисуненко Н.О., Бродніковський Д.М., Бродніковська І.В., Бричевський М.М., Васильєв О.Д. «Структурні, імпедансні та електронномікроскопічні дослідження багатошарових систем керамічного електроліту та анодного матеріалу». Наукова звітна сесія «Розвиток наукових засад отримання, зберігання та використання водню в системах автономного енергозабезпечення», Київ, грудень 2020: ІПМ НАНУ, с.19.
11. Полішко І.О., Лисуненко Н.О., Марек І.О., Смирнова-Замкова М.Ю., Бродніковський Д.М., Чедрик В.І., Бричевський М.М., Бродніковська І.В., Іванченко С.Е., Барановський Д.І , В’юнов О.І., Коваленко Л.Л., Янчевський О. З., Васильєв О.Д., Рагуля А.В., Білоус А.Г., Бродніковський Є.М. Міцність та електрична провідність цирконієво-оксидного електроліту стабілізованого оксидами церію та ітрію. Наукова звітна сесія «Розвиток наукових засад отримання, зберігання та використання водню в системах автономного енергозабезпечення», Київ, грудень 2020: ІПМ НАНУ, с.20.
12. Новохацька А.О., Акимов Г.Я., Коваленко Л.Л. «Вивчення електропровідних властивостей композитів катодного матеріалу для керамічних паливних комірок». Міжнародна школа-семінар для молодих вчених «Функціональні матеріали для технічних та біомедичних застосувань», Харків, Україна з 07 по 10 вересня 2020 р.
13. I. A. Rusetskyi, L. L. Kovalenko, I. A. Slobodyanyuk, M. O. Danilov, S. S. Fomanyuk, V. O. Smilyk, A. G. Belous, G.Ya. Kolbasov. Photoelectrochemical systems for hydrogen evolution using ion-conducting membranes. In Advanced Batteries Accumulators and Fuel Cells – 21st ABAF. Edited by Marie Sedlaříková, Vítězslav Novák, Tomáš Kazda and Petr Bača. Brno University of Technology Faculty of Electrical Engineering and Communication Department of Electrical and Electronic Technology. 2020, P. 66-68.