TARGETED COMPREHENSIVE PROGRAM SCIENTIFIC RESEARCH NAS OF UKRAINE

Development of scientific foundations for obtaining, storage and use of hydrogen in autonomous power supply systems

Elaboration and study of materials for anodes and interconnects of lightweight solid oxide fuel cells

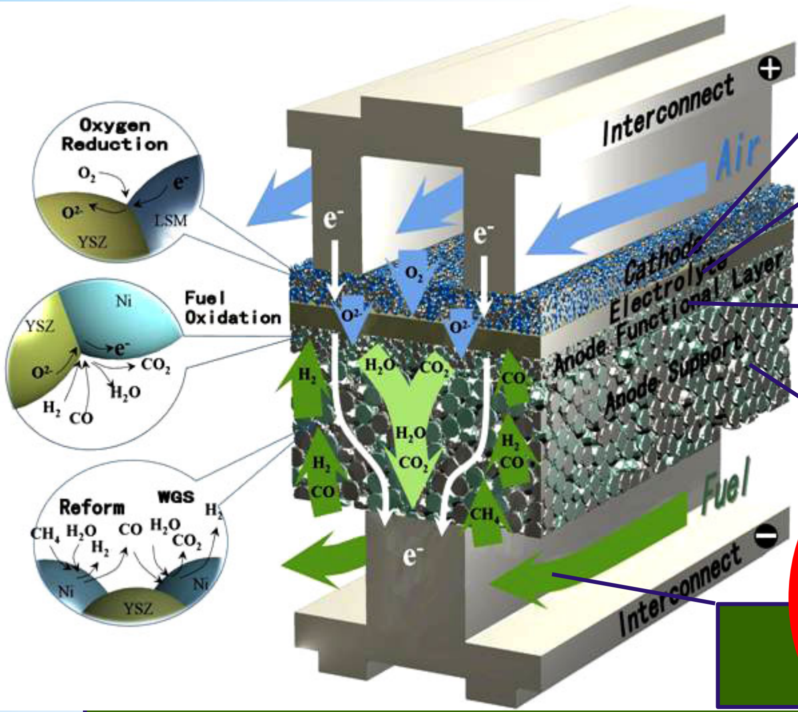
project № 15-21

Scientific adviser: Dr. Ostash O.P.
Performers: Vasyliv B.D. [1], V.Ya. Podhurska[1], O.D. Vasyliev[2], Ye.M. Brodnikovskii[2], I.O. Polishko[2], I.A. Danilenko[3], A.V. Shylo[3], T.A.Prikhna[4], Sverdun V.B.[4]
[1]Karpenko Physico-Mechanical Institute, NASU, Lviv, Ukraine
[2]Frantsevich Institute for Problems of Materials Science, NASU, Kyiv, Ukraine
[3]Donetsk Institute for Physics and Engineering, NASU, Kyiv, Ukraine
[4]Bakul Institute for Superhard Materials, NASU, Kyiv, Ukraine

The purpose of the research of the project was :

development of materials for anodes and interconnect elements of solid oxide fuel cells with increased resistance to operational degradation under the influence of hydrogen, impurities of hydrocarbon fuel and oxygen at a temperature of 600 ° C.

Solid Oxide Fuel Cell



Cathode

Electrolyte

Anode

Anode-substrate

Interconnect

Operative temperature:

800…1000 → 550…650 ºC;

Fuels:

H_2 → CO, CH_4 etc.

Anode reactions:

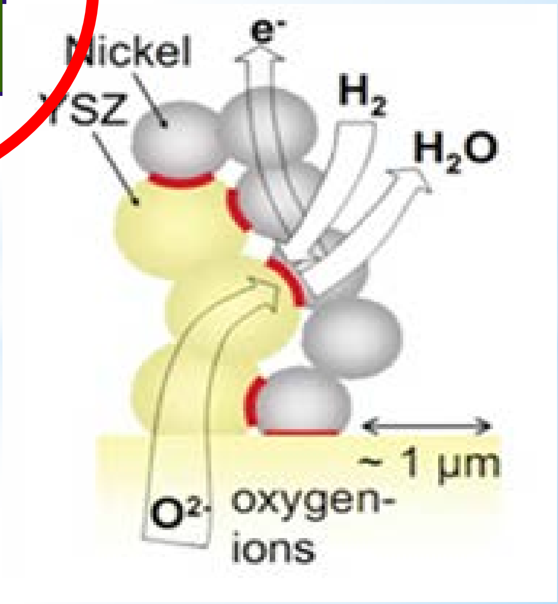
$H_2 + O^= \rightarrow H_2O + 2e^-$

$CO + O^= \rightarrow CO_2 + 2e^-$

$CH_4 + 4O^= \rightarrow 2H_2O + CO_2 + 8e^-$

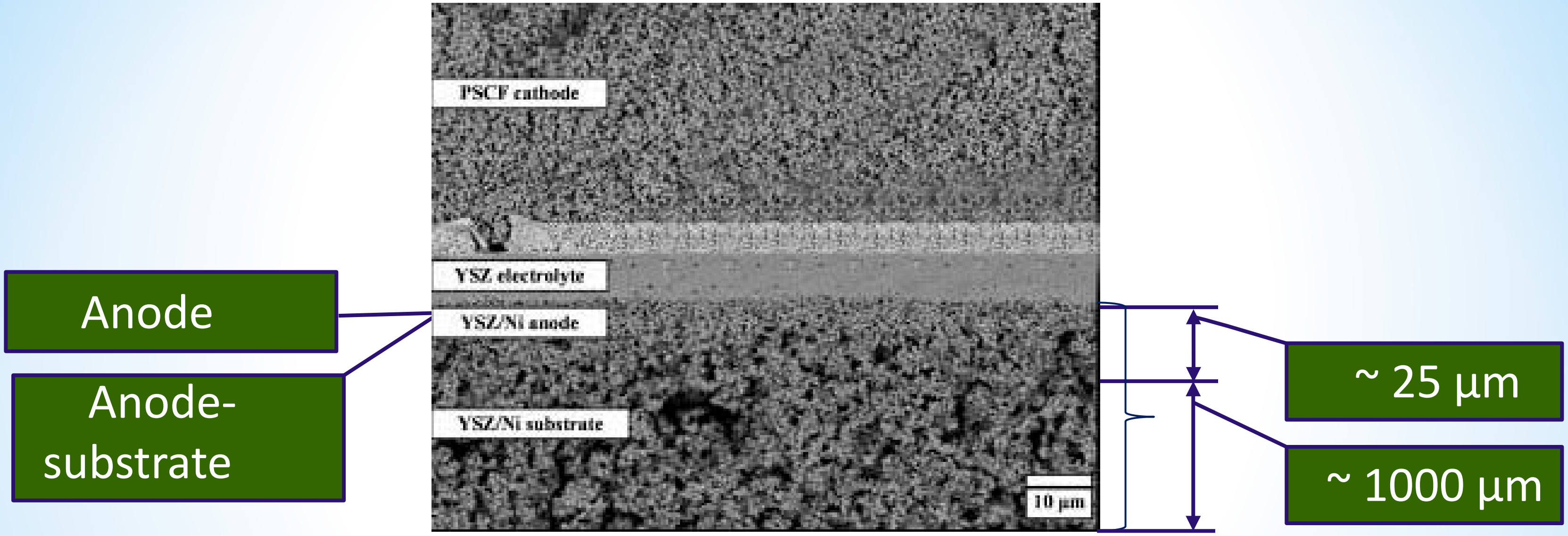
Cathode reaction:

$\frac{1}{2} O_2 + 2e^- \rightarrow O^=$



Requirements for the material of the anode-substrate

Functional layers of the fuel cell

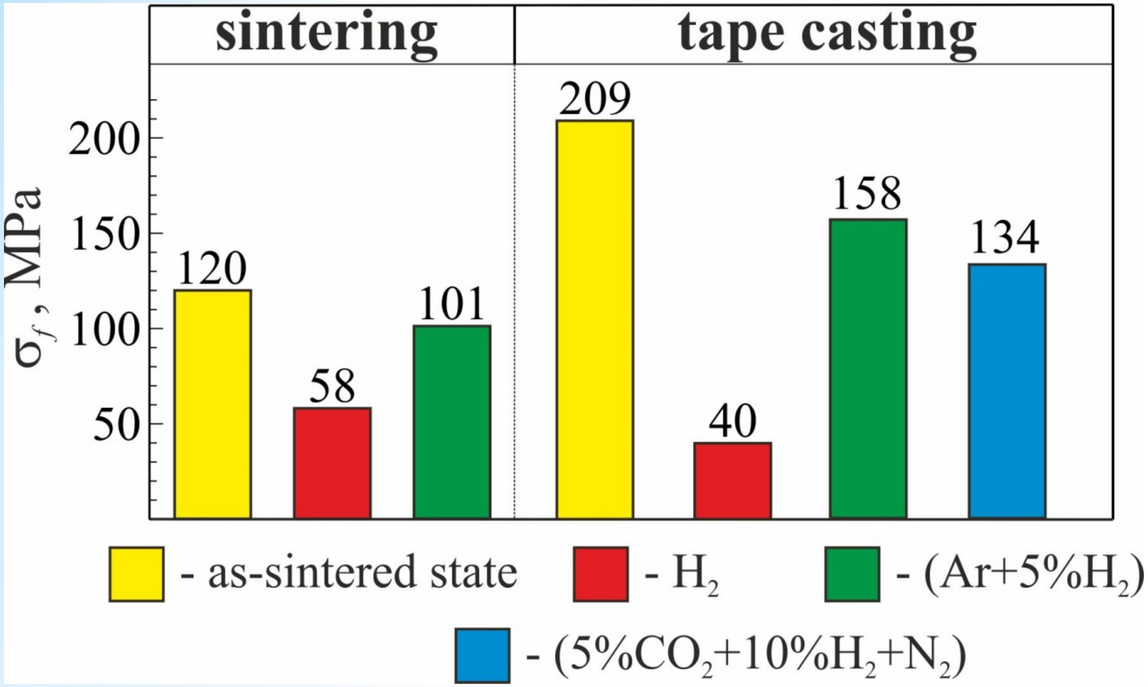


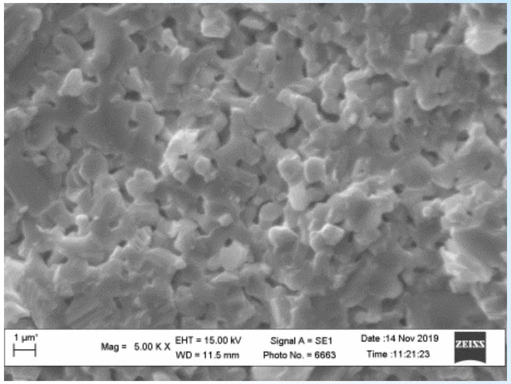
Haanappel V. A. C. , MaiA. , Uhlenbruck S. and Tietz F. Characterization of Anode-Supported Solid Oxide Fuel Cells With PSCF Cathode / J. Fuel Cell Sci. Technol. – 2008. - 6(1). – P. 011007-011007-6

- high electrical conductivity;
- the coefficient of thermal expansion is proportional to the ceramic materials of the anode, electrolyte and cathode (about $10{,}5 \cdot 10^{-6}$ К$^{-1}$);
- satisfactory strength (above 100 MPa);
- porosity 25…35 %.

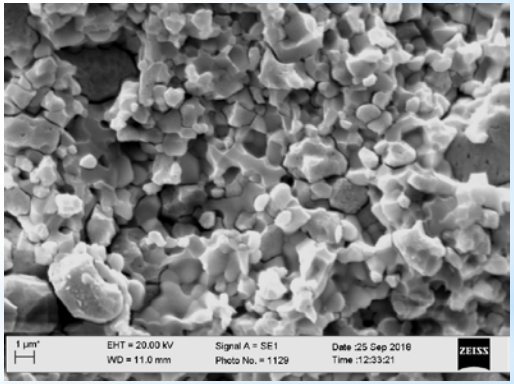
YSZ-NiO → YSZ-Ni

Material for anode substrate 8YSZ-NiO
(Institute for Problems of Materials Science)

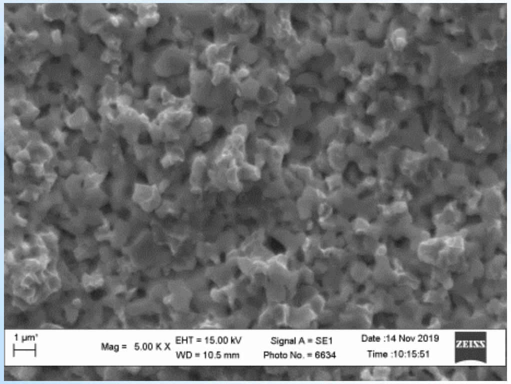




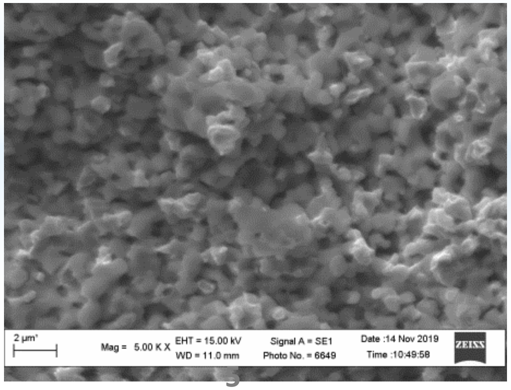
As-sintered state



Reduced in 100% H_2

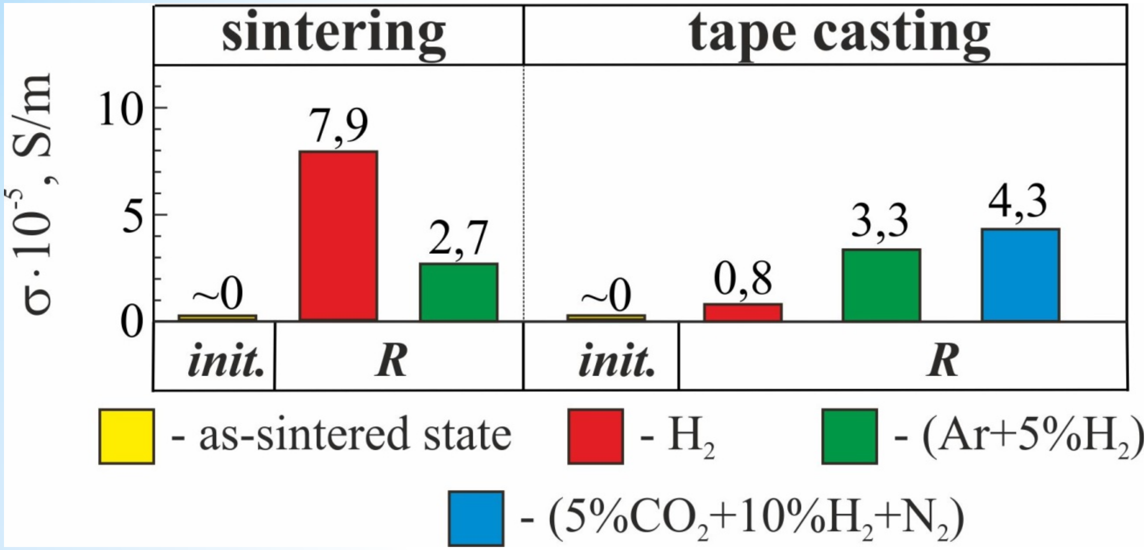


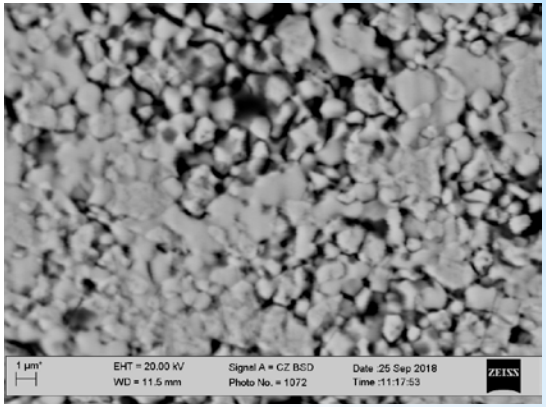
Reduced in $Ar+5\%H_2$



Reduced in $5\%CO_2+10\%H_2+N_2$

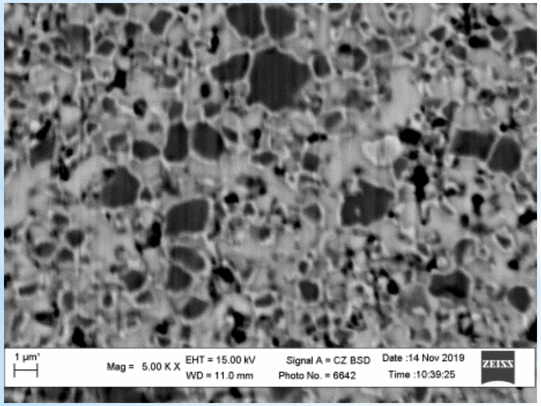
Material for anode substrate 8YSZ-NiO
(Institute for Problems of Materials Science)



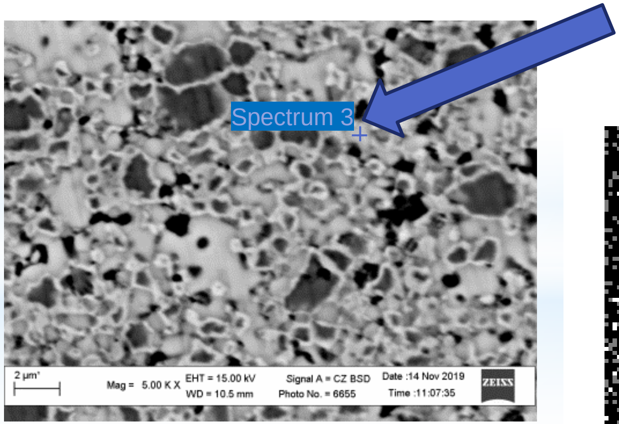


Reduced in 100%H_2

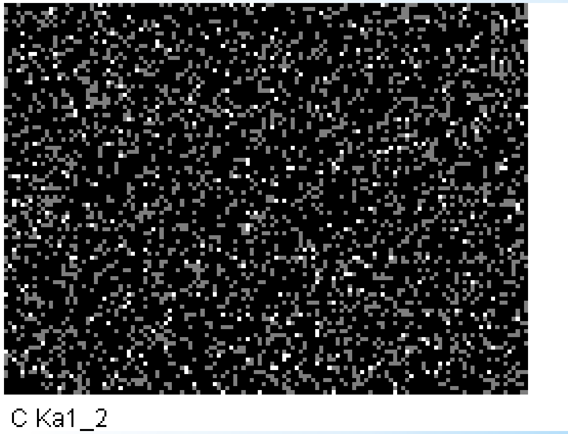
Element	Wt. %	At.%
C K	28.52	58.67
O K	16.89	26.08
Ni K	2.83	1.19
Y L	5.40	1.50
Zr L	46.36	12.56
Total	100.00	



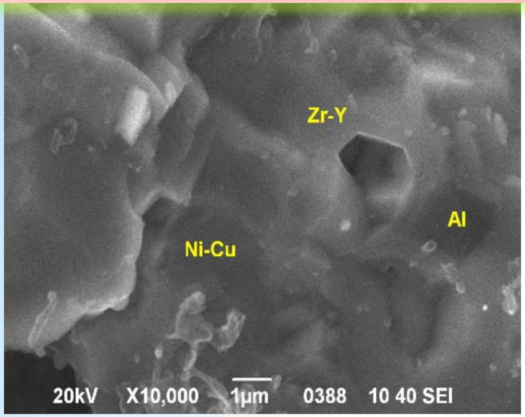
Reduced in Ar+5%H_2

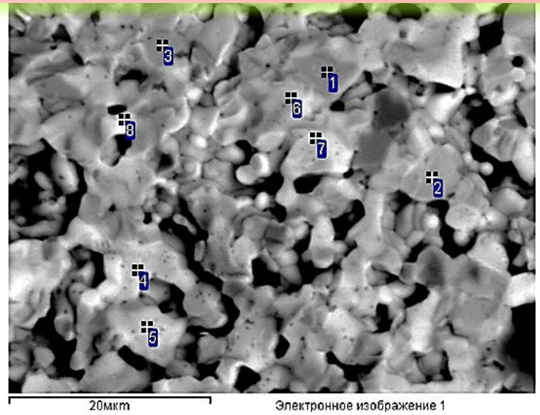


Reduced in 5%CO_2+10%H_2+N_2

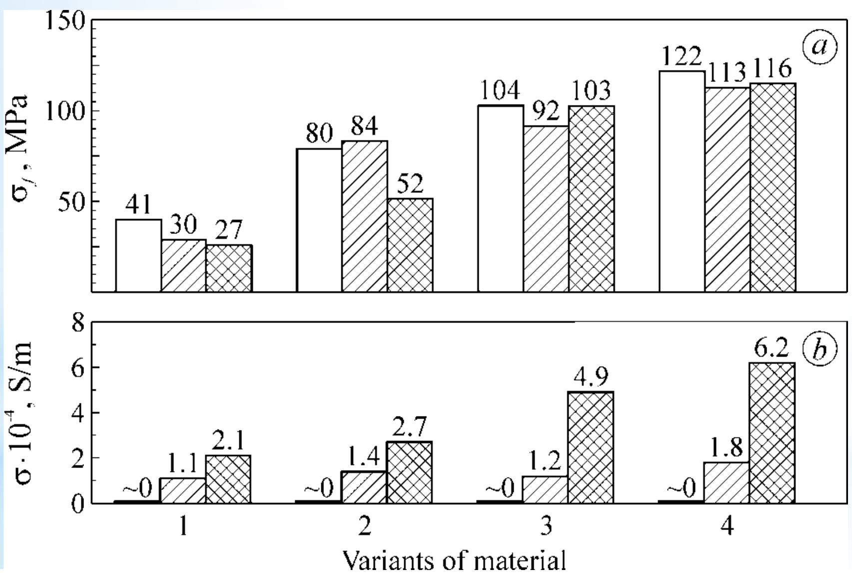


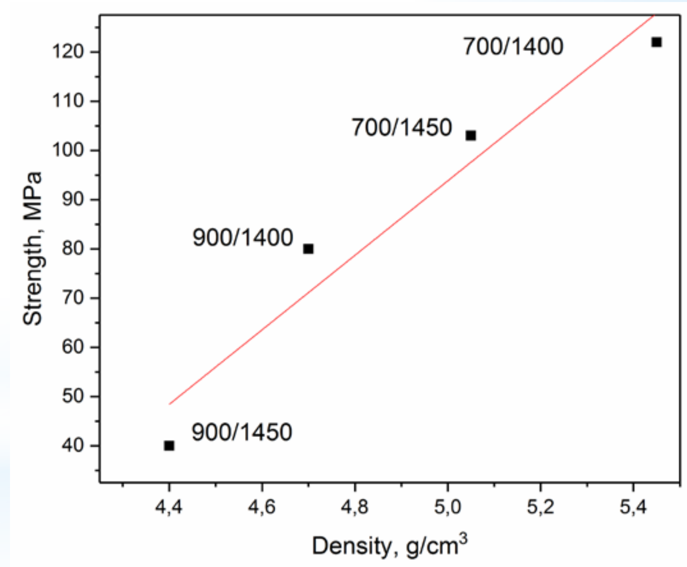
Material for anode substrate
50%(ZrO_2 – 8 mol%Y_2O_3 +2wt%Al_2O_3)+ 50% (NiO+5wt%CuO)
(Donetsk Institute for Physics and Engineering)





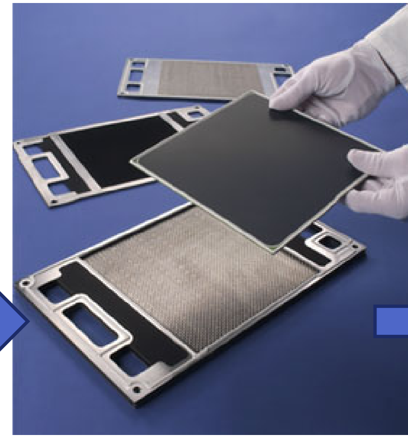
N	Al_2O_3	NiO	CuO	Y_2O_3	ZrO_2	HfO_2
1	0.63	86.64	11.76	0	0.97	0
2	0.69	86.34	10.01	0.40	1.83	0.73
3	0.03	85.30	10.60	0.42	3.28	0.37
4	0.63	4.20	0.44	11.39	81.19	2.16
5	1.60	4.78	0.85	10.15	80.97	1.65
6	0.52	5.15	0.74	11.09	80.98	1.51
7	2.19	6.05	1.06	11.82	77.90	0.97
8	0.69	8.41	1.73	10.17	77.52	1.47

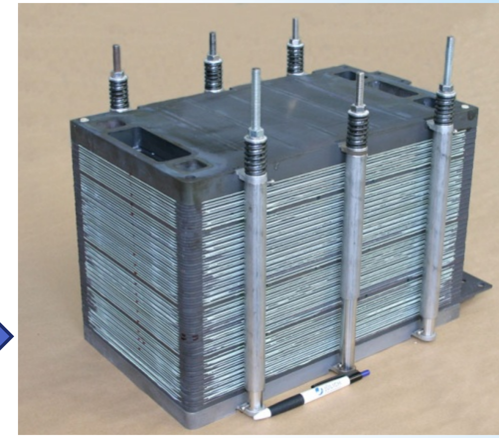




Strength σ_f (*a*) and specific electrical conductivity σ (*b*) of the investigated ceramics in as-sintered state (white bars) and the cermets after reduction at 600°C in Ar–5%H_2 mixture (hatched bars) and N_2–10%H_2–5%CO_2 mixture (cross-hatched bars): variant 1 – calcination temperature 900°C/sintering temperature 1450°C; variant 2 –900°C/1400°C; variant 3 –700°C/1450°C; variant 4 –700°C/1400°C.

Materials for interconnects





Requirements for interconnect materials

- resistance to high temperatures (~ 600 ºC);
- resistance to the effects of reducing and oxidizing media;
- high electrical and thermal conductivity;
- high strength;
- resistance to creep;
- the coefficient of thermal expansion is proportional to the ceramic materials of the anode, electrolyte and cathode (about $10{,}5 \cdot 10^{-6}\ K^{-1}$);
- good workability;
- **low density (important for the automotive and aerospace industries)**.

Traditional materials for interconnects

Chromium ferritic steels : **Crofer**, AISI 430, AISI 441, IT-11

Component composition of Crofer steels:

Characteristic	Value
Conductivity, S/m:	$9,7 \cdot 10^5$
Thermal conductivity, Wt/(m · K):	25,4
Coefficient of linear expansion, K^{-1}:	$11,2 \cdot 10^{-6}$

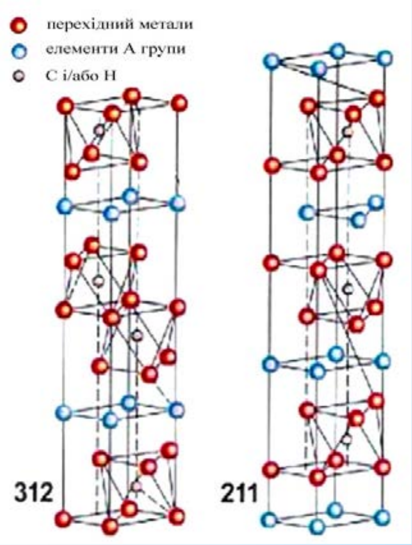
Alternative materials for interconnects

MAX phases-based composites

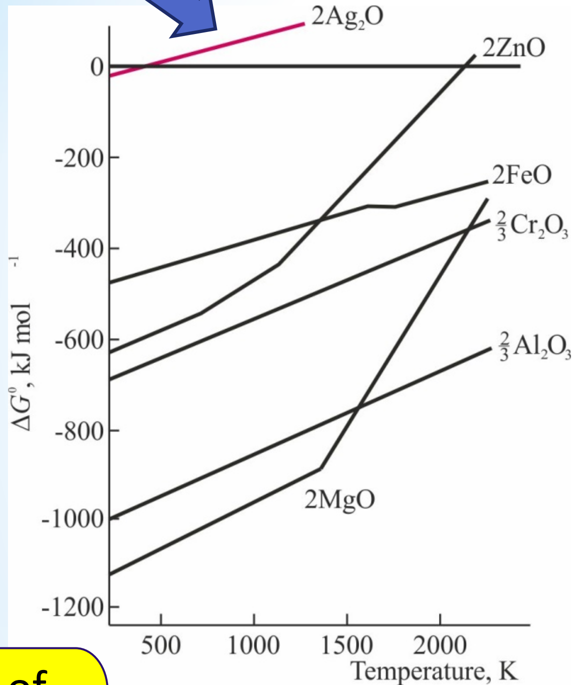
MAX-phase:

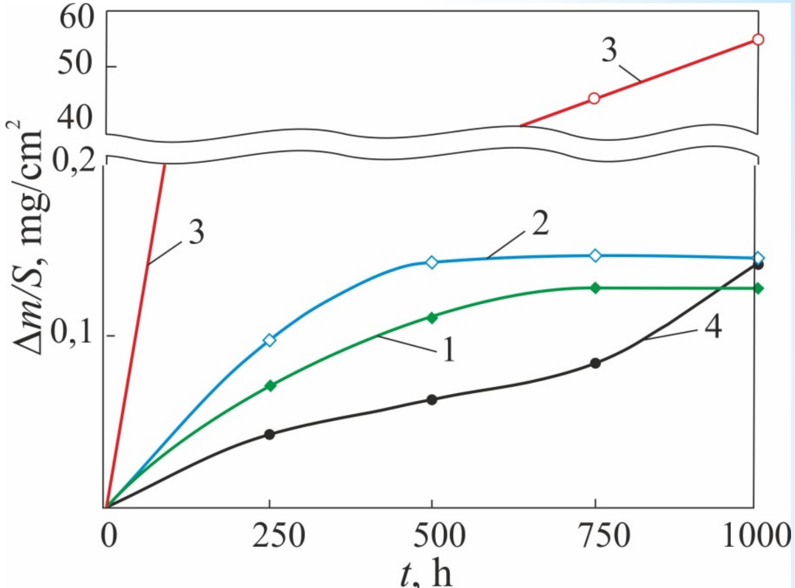
$M_{n+1}AX_n$, where n=1÷3

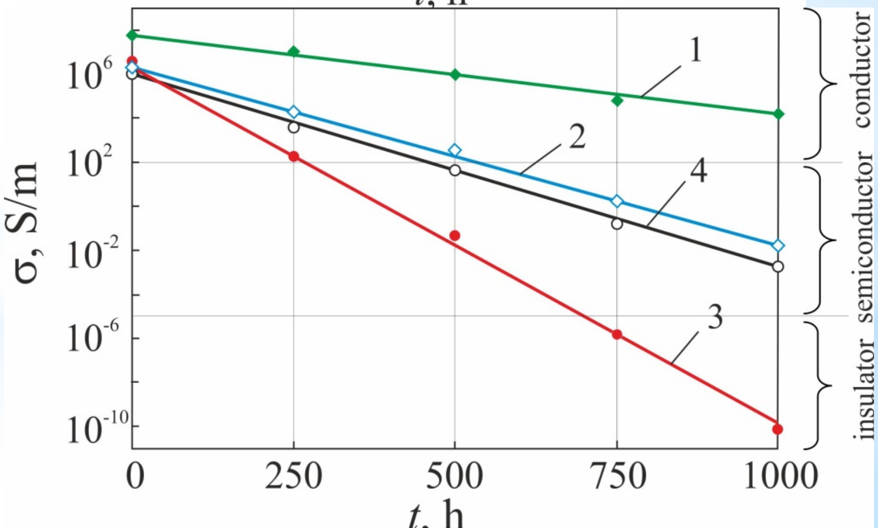
Characteristic	Value
Conductivity, S/m:	$2,2 \cdot 10^6$
Thermal conductivity, Wt/(m · K):	46,0
Coefficient of linear expansion, K^{-1}:	$9,0 \cdot 10^{-6}$
Density, g/sm³:	**4,3**



Improving the oxidation resistance and electrical conductivity of materials for SOFC interconnects



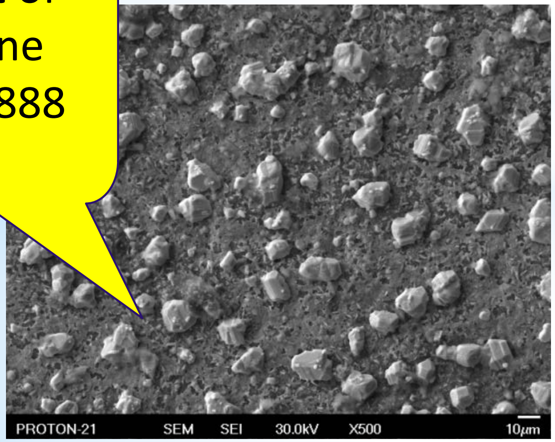




1 - Ti_2AlC+Ag 2 - Ti_2AlC 3 - Ti_3AlC_2

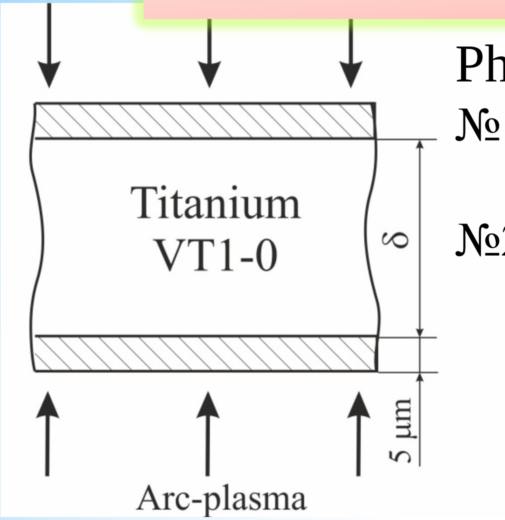
4 - Crofer steel

Patent of Ukraine №137888



Surface after 1000 hours at 600°C

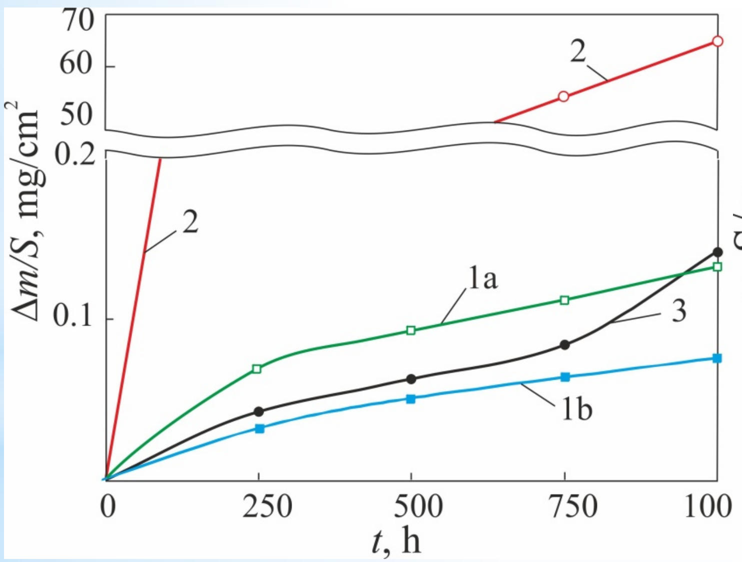
Thin interconnects

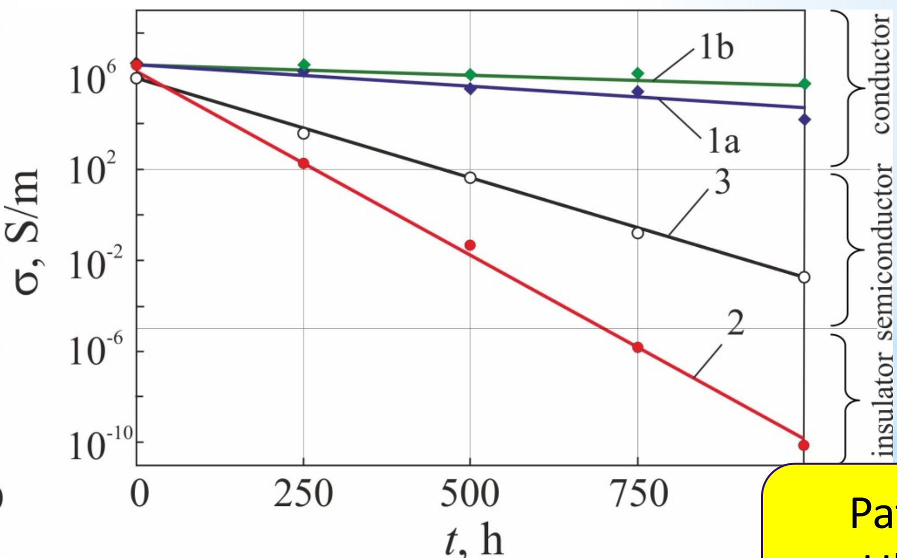


Phase composition of targets:
№1 - 95,3% Ti_2AlC;
4,7% TiC
№2 – 77,6% Ti_2AlC;
17,5% Ti_3AlC_2;
4,4% Al_2O_3;
0,5% TiC

Phase composition of the surface after oxidation:
№1 – 42,6 Ti_2AlC;
19,7 Ti_3Al;
19,6 Ti_3AlC;
18,1 (Ti, Al)C
№2 – 46,8 $TiAl_2$
23,6 Ti_2AlC;
17,5 (Ti, Al)C; 12,1 α-Ti.

δ = 0,06 mm; δ = 0,5 mm.





1a – coating MAX phase at 0.5 mm Ti, 1b - coating MAX phase at 0.06 mm Ti, 2 – Ti_3AlC_2, 3 – Crofer steel.

“A production method of the thin interconnects for solid oxide fuel cells”

Patent of Ukraine №121831

CONCLUSION

- It was found that 8YSZ–NiO ceramics obtained by the tape casting technology is more promising for the production of SOFC anode substrates than one obtained by sintering powders. After its one-time reduction in the presence of carbon dioxide in a hydrogen-containing environment (N_2–10%H_2–5%CO_2), strength of 8YSZ–Ni cermet decreases by 15% compared to that reduced in Ar–5%H_2 mixture. This is due to the deposition of carbon at the ZrO_2–Ni interphases.
- Technological modes for production of ceramics of 50% (ZrO_2 – 8 mol%Y_2O_3 – 2 wt% Al_2O_3) + 50% (NiO – 5 wt% CuO) composition were optimized in terms of the temperatures of calcination of powders (700°C) and their sintering (1400°C), which allowed to obtain a fine-grained microstructure and increased both strength and electrical conductivity of the corresponding cermet. After reduction in N_2–10%H_2–5%CO_2 gas mixture, the cermet does not lose its mechanical properties compared to the as-sintered ceramics. This ceramic is promising as anode material for a SOFC operating, for example, on syngas.
- High oxidation resistance and electrical conductivity in high-temperature (600°C) oxidizing medium is demonstrated by the coating of the Ti–Al–C system, applied by arc – plasma method on a thin (0.5 mm) titanium plate of the VT1-0 brand. This is due to the formation of oxidation-resistant and electrically conductive phases of Ti_3AlC (with antiperovskite crystal structure) and TiAl and Ti_3Al. On this basis, you can create light interconnections SOFC as an alternative to those used from steel type Crofer, which will significantly (~ 50%) reduce the weight of batteries SOFC.

PUBLICATION

According to the results obtained during the project №15 (2019-21)
4 articles and 11 abstracts of conferences were published, 2 patents of Ukraine were obtained.

1. Vasyliv B.D., Podhurska V.Ya., Ostash O.P., Polishko I.O., Brodnikovs'kyi E.M., Ivanchenko S.E., Vasyl'ev O.D. Influence of the working media of fuel cells on the structure and physicomechanical characteristics of ceramics of the ZrO_2–Y_2O_3–NiO system // **Materials Science**. – 2020. – 56, № 1. – P. 15–21.
2. Podhurska V.Ya., Vasyliv B.D., Ostash O.P., Danilenko I.A., Shylo A.V., Burkhovetsky V.V. Influence of the reducing media on the structure and physicomechanical properties of ceramics of the ZrO_2–Y_2O_3–Al_2O_3–NiO–CuO system // **Materials Science**. – 2021. – **56**, № 6. – P. 843–851.
3. Vasyliv B., Podhurska V. Development of the concept of a spheroidal shape anode for a solid oxide fuel cell // In: Ikhmayies S. (eds) **Advances in Energy Materials.** Advances in Material Research and Technology. Springer, Cham, 2020, pp. 77–103. https://doi.org/10.1007/978-3-030-50108-2_4
4. Podhurska V., Brodnikovskyi D., Vasyliv B., Gadzyra M., Tkachenko S., Čelko L., Ostash O., Brodnikovska I. ,. Brodnikovskyi Ye, Vasylyev O. . Ti-Si-C in-situ composite as a potential material for lightweight SOFC interconnects, **Promising Materials and Processes in Applied Electrochemistry**, edited by V.Z. Barsukov, Yu.V. Borysenko, V.G. Khomenko, O.V. Linyucheva, Kyiv,KNUTD, 2020, pp. 54–68. https://er.knutd.edu.ua/handle/123456789/17000
5. Ostash O.P., Prikhna T.O., Podhurska V.Ya., Sverdun V.B., Vasyliv B.D. Material for manufacturing of interconnect elements of solid oxide fuel cells. **UA patent** No. 137888, published Nov 11, 2019, bull. No.21.
6. Ostash O.P., Prikhna T.O., Kuprin O.S., Podhurska V.Ya., Sverdun V.B., Vasyliv B.D. A production method of the thin interconnects for solid oxide fuel cells, **UA patent** No.121831, published July 27, 2020, bul. No.14.

**Фізико-механічний інститут
ім. Г.В. Карпенка НАН України**

Дякуємо за увагу

**H.Karpenko Physico-Mechanical Institute, NASU,
5 Naukova str., 79060 Lviv,
Ukraine**

Thank you for attention