TARGET COMPREHENSIVE PROGRAM
SCIENTIFIC RESEARCH NAS of UKRAINE

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

«DEVELOPMENT OF TAPE CASTING TECHNIQUE REGIMES FOR MANUFACTURING OF SOLID OXIDE FUEL CELLS»

project № 18

STRUCTURAL, IMPEDANCE AND ELECTRON MICROSCOPIC STUDIES OF MULTILAYER SYSTEMS FOR LOW-TEMPERATURE (600 °C) FUEL CELL

project № 17

Y. Brodnikovskyi [1], Vasylyev O.[1], Polishko I.[1], Ivanchenko S.[1], Lysynenko N.[1], Kovalenko L.[2], Brodnikovskyi D.[1], Chedryk V.[3], Brodnikovska I.[1], Horda R.[4], Smyrnova-Zamkova M. [1], Marek I. [1], Myslyvchenko O.[1], Vyunov O.I.[2], Yanchevsky O.Z. [2], Ragulya A[1], Orlyk S[3], Belous A. [2], Vereshchak V[5], Nosyk A[6].

[1] *Frantcevych Institute for Problems of Materials Science, Ukraine*

[2] *Vernadsky Institute of General and Inorganic Chemistry, Ukraine*

[3] *Pisarzhevskii Institute of Physical Chemistry, Ukraine*

[4] *Ovcharenko Institute of Biocolloidal Chemistry, Ukraine*

[5] *Ukrainian State University of Chemical Technology, Ukraine*

[6] *Zirconia Ukraine Ltd., Ukraine*

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OUTLINE

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- Development of stabilized zirconia powders
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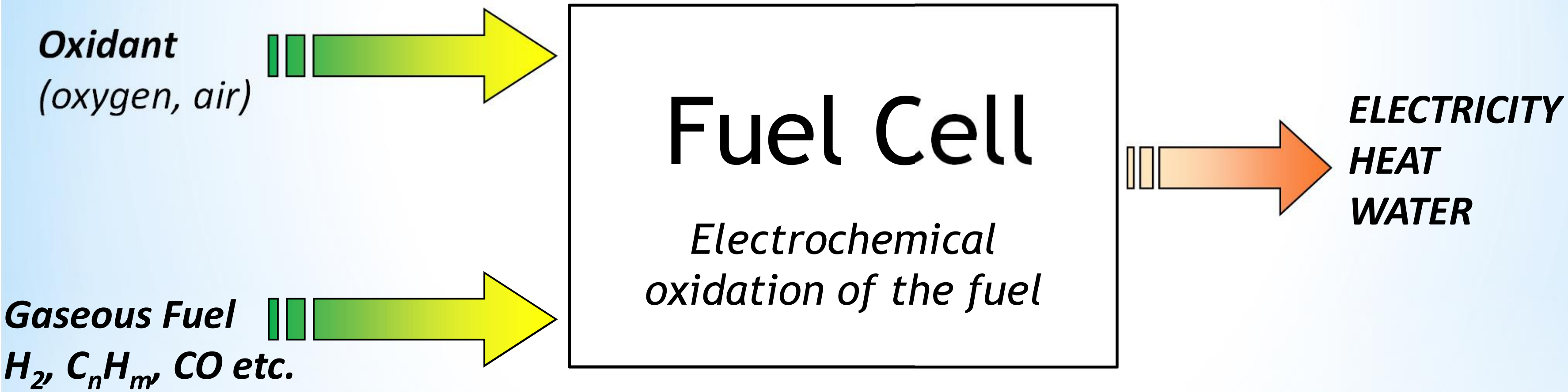
- Properties of the ceramic samples made from synthesized zirconia powders: 8Ce2YSZ, 8YSZ, 3YSZ, 10YbSZ, 10EuSZ, 10GdSZ, 10SmSZ

General operation scheme of FC

Fuel Cell (FC) - device which **directly** convert chemical energy of fuel and oxidant into electrical energy, heat with the highest efficiency and low environmental pollution



Total efficiency = 80-90 %!!!

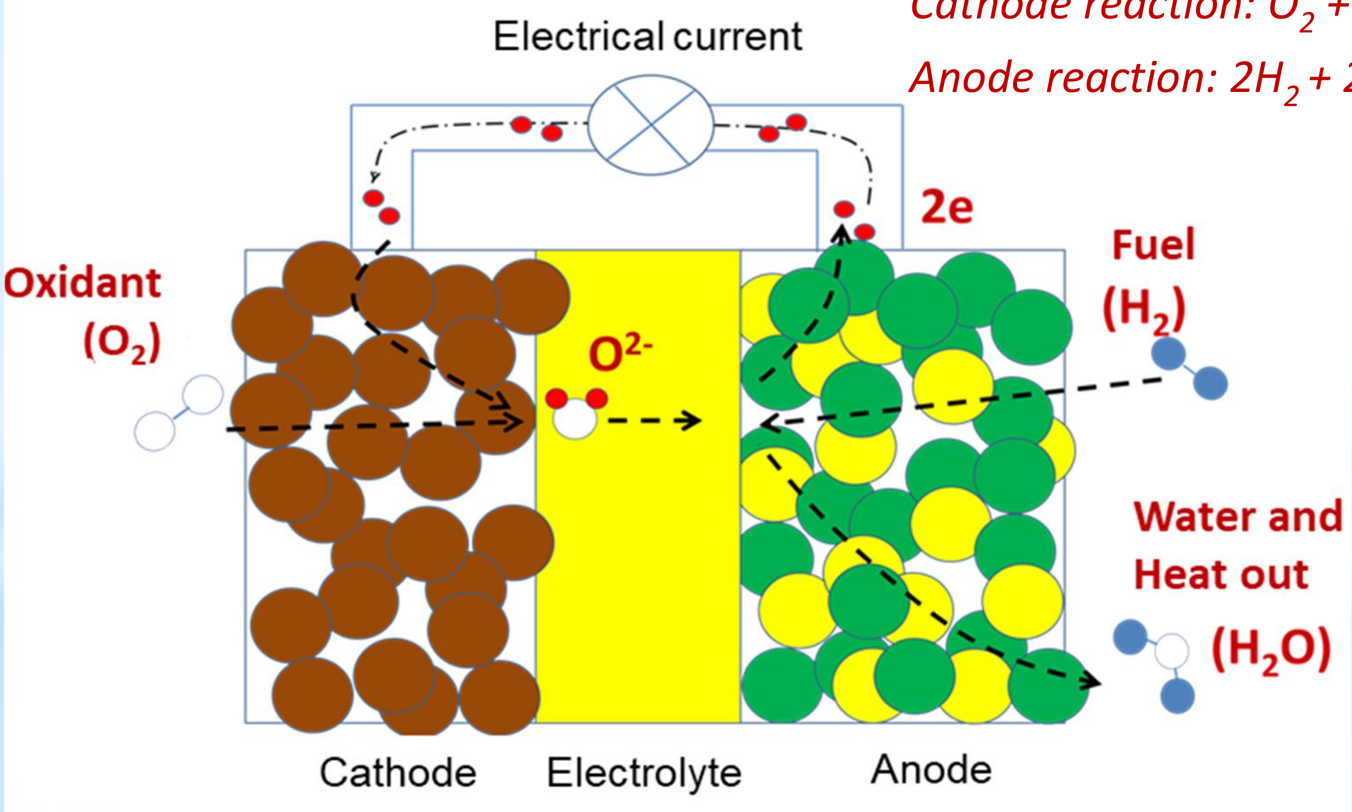
Up to 65 % (electrical energy) + ~30 % (heat energy)

Operation principles of SOFC

- *The oxygen that has entered the fuel cell at the cathode reacts with the electrons that have traveled from the anode to the cathode through the external circuit to form oxide ions (O^{2-}).*
- *Oxide ions travel to the anode, react with hydrogen, and form water, while releasing electrons.*
- *The electrons travel through the external circuit to the cathode and repeat the same reaction process:*

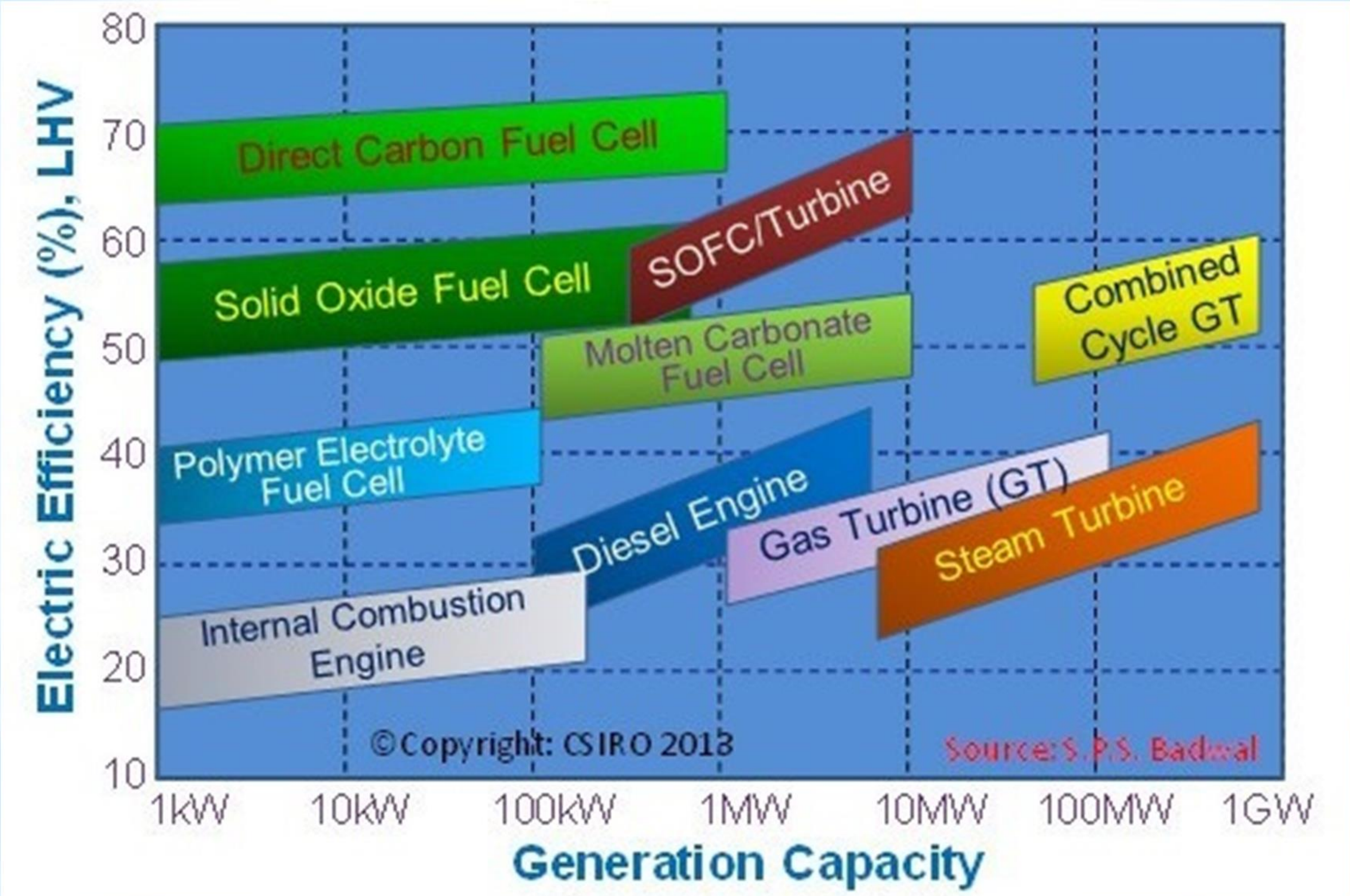
Cathode reaction: $O_2 + 4e^- \rightarrow 2O^{2-}$

Anode reaction: $2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$



Total reaction: $2H_2 + O_2 \rightarrow 2H_2O + Q + E$

The electric efficiency versus power plant size for different power generation technologies



SOFC is promising technology for power production!

https://csiropedia.csiro.au/ceramic-fuel-cells/

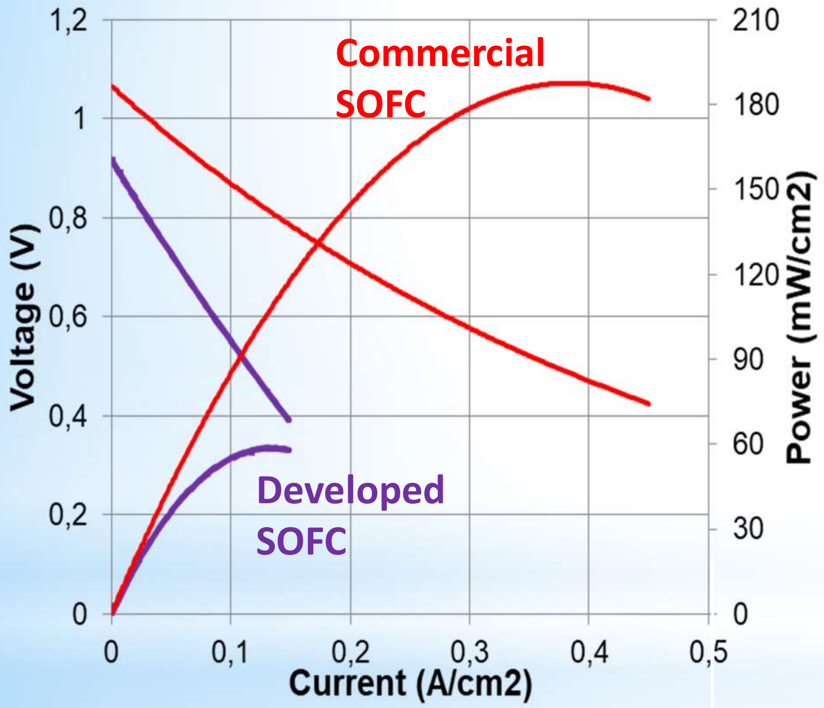
SOFC Advantages:

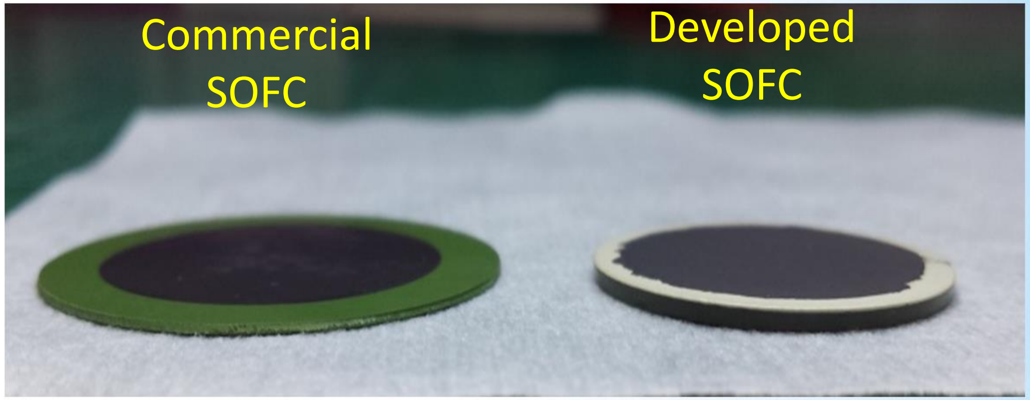
- ✓ The Highest efficiency at any scale (electricity[65%] + heat) even compering with other types of FC;
- ✓ Fuel flexibility (C_nH_m, syngas, H_2, CO can be used as fuels);
- ✓ Inexpensive catalyst (Ni);
- ✓ Modular principle (easy to scale up systems from kW to MWs)
- ✓ Low noise (no moving parts);
- ✓ Environmentally friendly (zero or near-zero emissions);
- ✓ Production of water as a byproduct of electrochemical reaction.
- ✓ Decentralization of energy supply system;

***SOFCs are the most promising class of fuel cells** due to their highest efficiency among other fuel cell types, flexibility of the fuel choice (C_mH_n, CO, H_2 etc.) and have no needs in noble materials for catalyst application.*

Background

Project FP7 NANOMATEPC №608906,
«Deployment of Socially Beneficial Nano and Material Technologies in European Partnership Countries»





SOFC type	*Thickness, μ*		
	electrolyte	*anode*	*cathode*
Commercial SOFC	*10-15*	*370-400*	*15-20*
Developed SOFC	*25-30*	*900-1000*	*10-12*

Development of tape-casting technique for SOFC production

Tape casting is a fabrication technique to produce thin ceramic sheets from ceramic slurry that casted in a thin layer onto a flat surface, and then dried and sintered.

Motivation:

- ✓ ***Tape casting is a relatively simple technique****, which allows to manufacture thin elastic tapes of high density with predetermined thickness and uniform distribution of powder in a volume of the tape.*
- ✓ *The method is widely used as a basis for manufacturing of many modern electronic devices and permanently upgraded;*
- ✓ ***Tape-casting technique is practically industrial method which can be easily to scale-up****!*

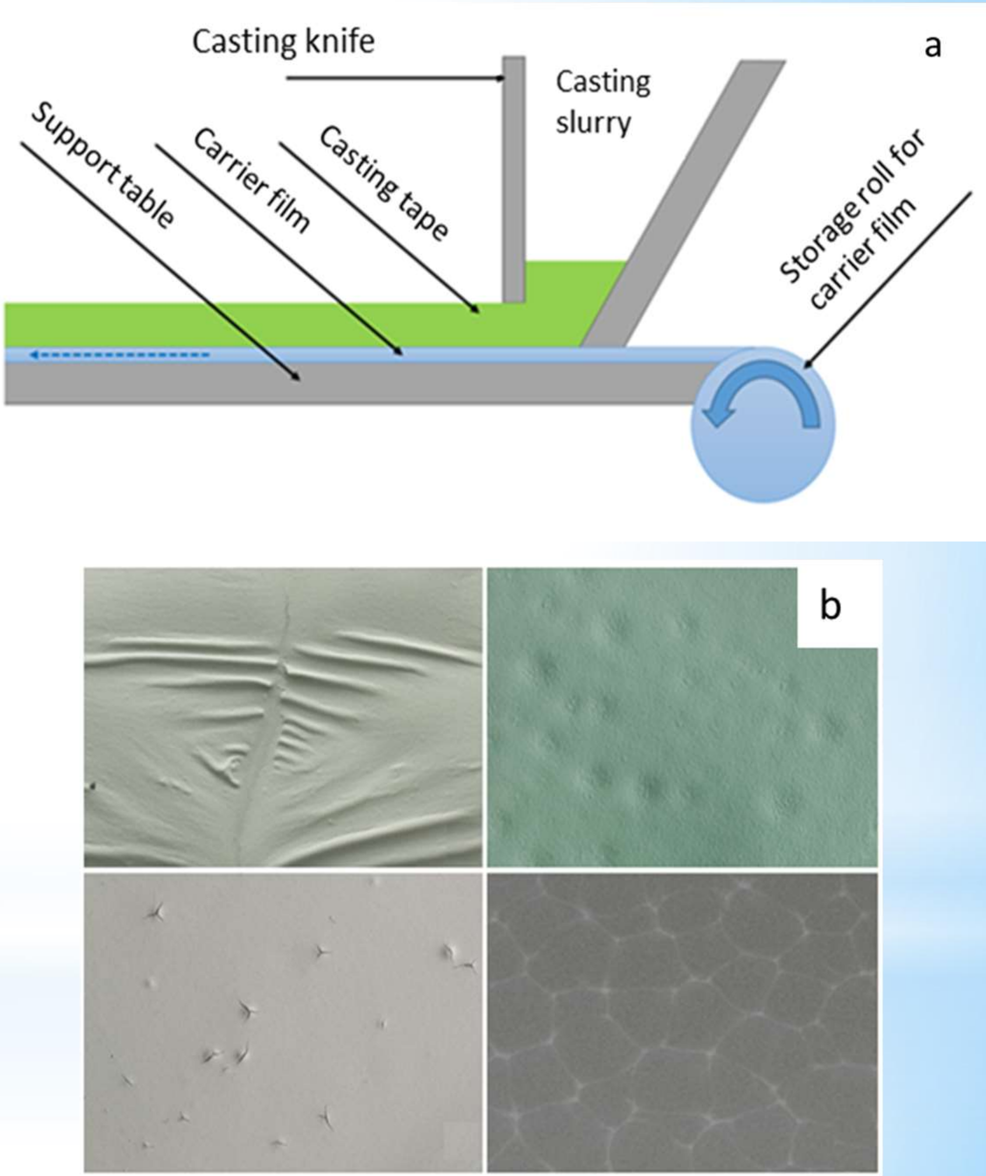


Figure. Principal scheme of tape casting technique (a) and CEM images of examples of the casted tape defects (b).

Development of stabilized zirconia powders

Motivation:

- ✓ *Ukrainian zircon deposit is ~10 % of the World natural resources;*
- ✓ *Zirconia powders can be used for different applications*

  - ➢ *The laboratory method for production of zirconia powders with different stabilizers (8YSZ, 8Ce2YSZ, 1Ce10ScSZ, 10EuSZ, 10SmSZ, 10YbSZ, 10GdSZ and others) was developed.*
  - ➢ *The developed zirconia powder (8YSZ) were produced in necessary quantities to elaborate the tape casting technique for production of the SOFC anode and electrolyte films.*
  - ➢ *Also different stabilized zirconia powders were used for preparation of the ceramic samples to study their electrical and mechanical properties.*

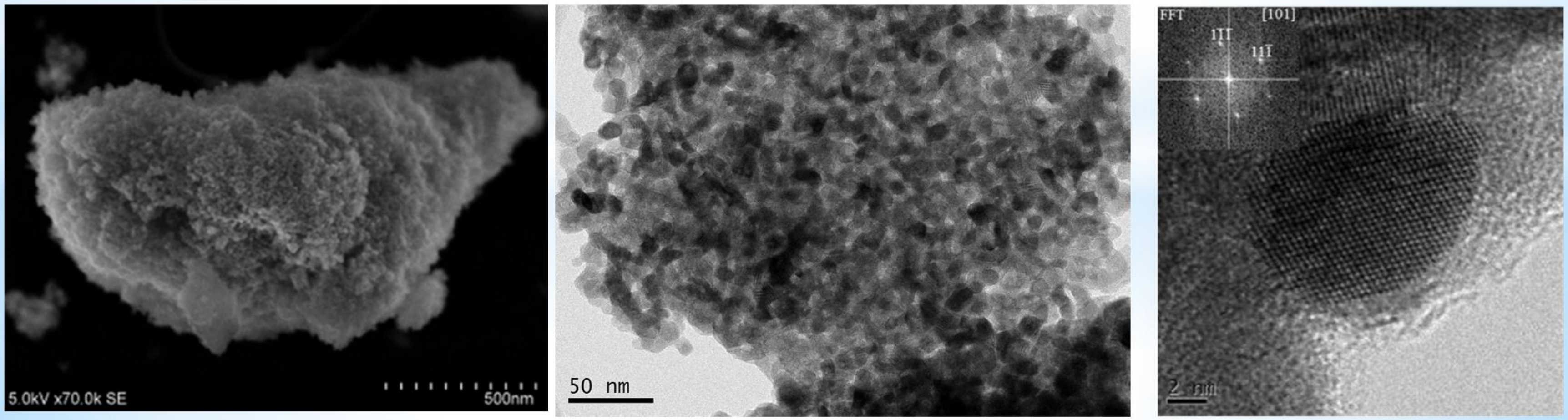


Figure. TEM images of the synthesized zirconia powders.

Development of tape-casting technique for SOFC production

- *Suspension recipes with an optimal component composition for manufacturing of non-defect types for SOFC anode and electrolyte were formulated.*
- *It was found that increasing the viscosity of the suspensions will result in thicker and stronger tapes, however, high viscosity creates difficulty in mixing and increases the suspension irretrievable losses.*
- *The control of anode and electrolyte film thickness could be achieved by step-by-step lamination of thin films. The obtained tapes were successfully laminated and sintered into an SOFC*

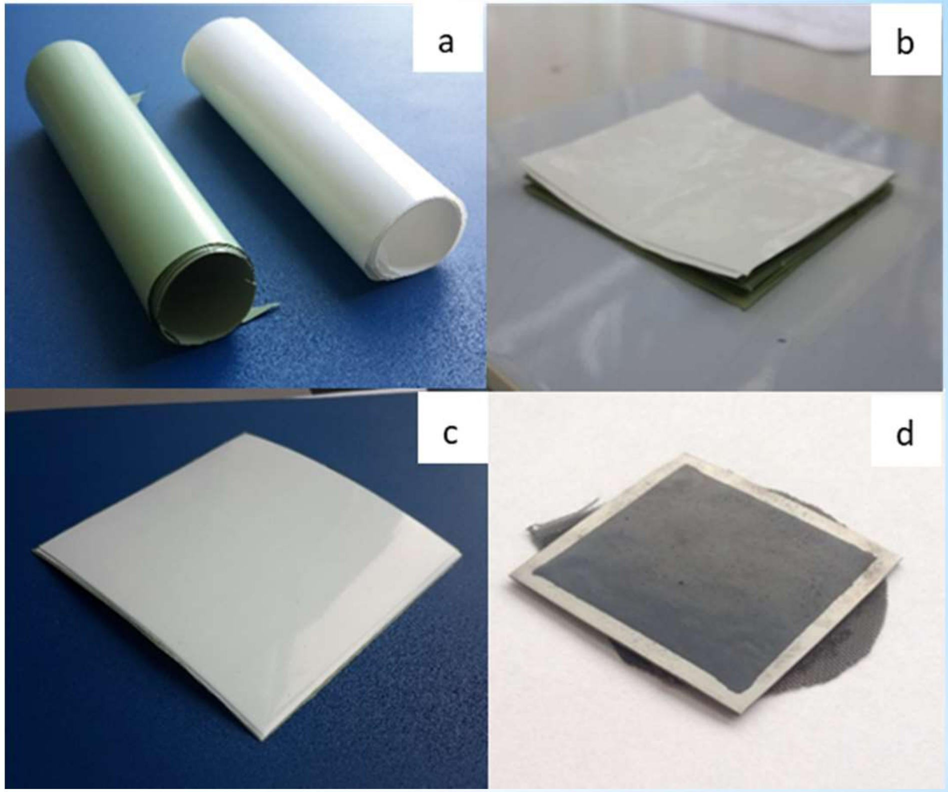
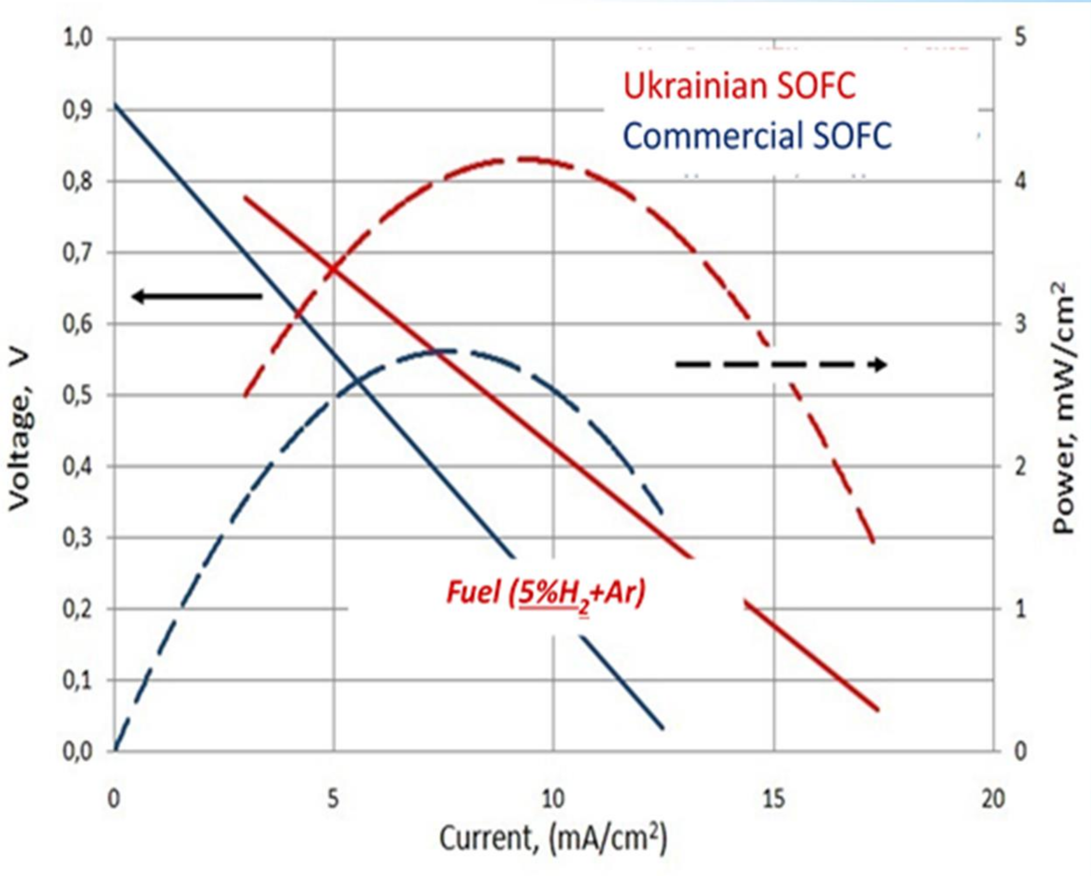


Figure. Type casted films of anode (green) and electrolyte (white) (a); cut anode and electrolyte types into square-shaped samples for further half-cell preparation (b); laminated types in half-cell (c); sintered SOFC (d); drying of just casted anode type (e).

Comparison of the developed SOFC with commercial one

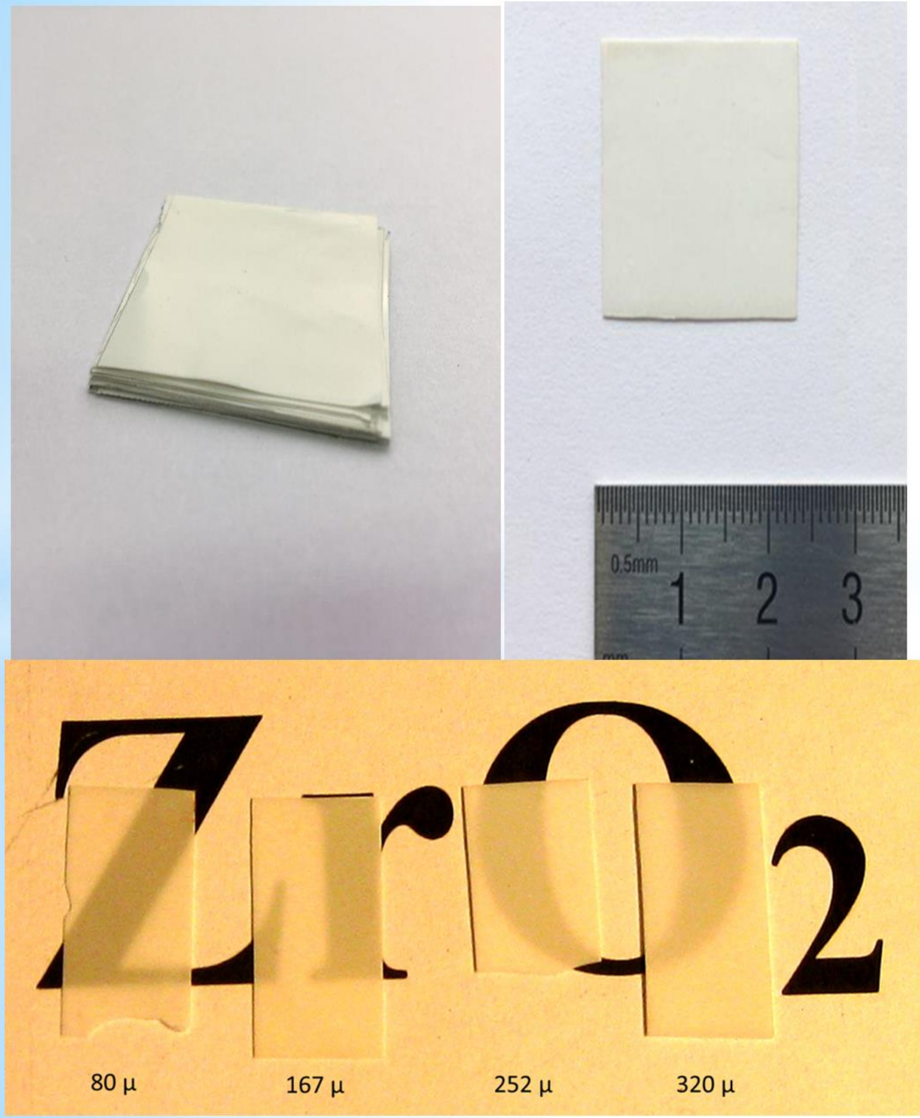
The tape-casted SOFC (electrolyte 8YSZ, anode NiO – 8YSZ, cathode LSM – 8YSZ) made using elaborated laboratory technology and commercially available anode-supported SOFC (electrolyte 8YSZ, anode NiO – 8YSZ, cathode LSM – 8YSZ) were tested with the stand for measuring of fuel cells electrical properties ("Scribner Teledyne Medusa RD 890CL" USA), at the same conditions.

The tests of SOFC were performed at 800 °C, and fuel mixture 5 % H_2 – 95 % Ar and air were fed into the anode and the cathode, respectively.



The SOFCdeveloped demonstrates much higher level of power density (4.2 mW/cm²) in comparison with the commercial one (2.8 mW/cm²) at the same testing conditions (800 °C, 5 % H_2+Ar, air).

Development of tape-casted 8YSZ electrolyte samples

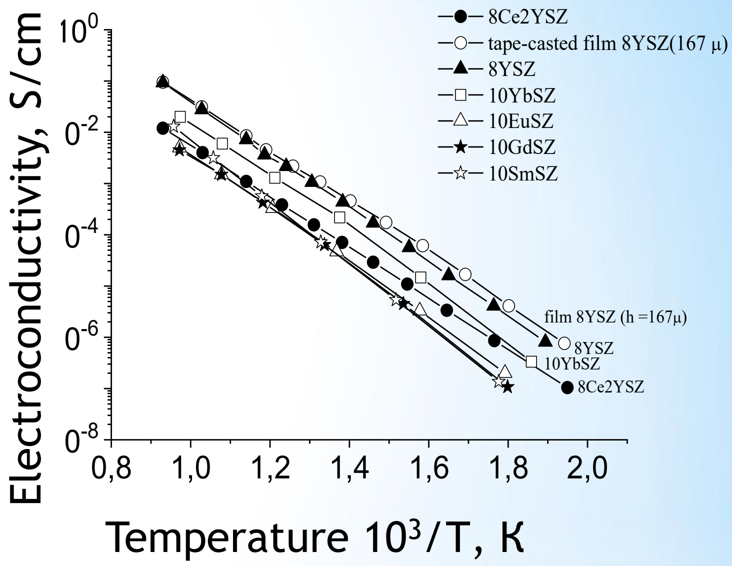


Sample/thickness	Electrical conductivity at 600°C, S/cm	Activation Energy, eV
Zirconia ZrO_2 stabilized with 8 mol.% Y_2O_3		
Tape-casted film/80 µ	$8{,}5 \cdot 10^{-3}$	1,04
Tape-casted film/167 µ	$7{,}1 \cdot 10^{-3}$	1,03
Tape-casted film/252 µ	$6{,}5 \cdot 10^{-3}$	1,015
Tape-casted film/320 µ	$5{,}8 \cdot 10^{-3}$	1,0
Pressed ceramic samples/ 800 µ	$5{,}2 \cdot 10^{-3}$	0,98

- ✓ *Dried tape-casted films had thickness about 25-50 µ;*
- ✓ *The sintered ceramic sample thickness was managed by quantity of the tape-casted films;*

Electrical conductivity of the ceramic samples: 8Ce2YSZ, 8YSZ, 3YSZ, 10YbSZ, 10EuSZ, 10GdSZ, 10SmSZ

Method of synthesis	Material	Activation Energy, eV	Electrical conductivity at different temperatures, S/cm		
			600°C	700°C	800°C
Hydrothermal	8Ce2YSZ	1,015	$1{,}1\cdot10^{-3}$ $(1{,}3\cdot10^{-3})$*	$4\cdot10^{-3}$ $(4{,}5\cdot10^{-3})$*	$1{,}2\cdot10^{-2}$ $(1{,}4\cdot10^{-3})$*
Co-precipitation	3YSZ	-	$1\cdot10^{-3}$	-	-
	8YSZ	0,98	$5{,}2\cdot10^{-3}$	$2{,}7\cdot10^{-2}$	$9{,}3\cdot10^{-2}$
	8YSZ (film, h = 167 μ)	1,03	$8{,}5\cdot10^{-3}$	$3{,}1\cdot10^{-2}$	$9{,}5\cdot10^{-2}$
	10YbSZ	1.067	$3\cdot10^{-3}$ $(5{,}6\cdot10^{-3})$*	$1{,}1\cdot10^{-2}$ $(2{,}1\cdot10^{-2})$*	$3{,}5\cdot10^{-2}$ $(6{,}5\cdot10^{-2})$*
	10EuSZ	1.065	$6{,}7\cdot10^{-4}$ $(1{,}4\cdot10^{-3})$*	$2{,}5\cdot10^{-3}$ $(5{,}3\cdot10^{-3})$*	$9\cdot10^{-3}$ $(1{,}9\cdot10^{-2})$*
	10GdSZ	1.11	$6{,}3\cdot10^{-4}$ $(1{,}2\cdot10^{-3})$*	$2{,}5\cdot10^{-3}$ $(4{,}8\cdot10^{-3})$*	$8{,}5\cdot10^{-3}$ $(1{,}6\cdot10^{-2})$*
	10SmSZ	1.2	$9\cdot10^{-4}$ $(1{,}7\cdot10^{-3})$*	$5\cdot10^{-3}$ $(9{,}6\cdot10^{-3})$*	$2\cdot10^{-2}$ $(3{,}8\cdot10^{-2})$*



* In order to compare conductivities of ceramic samples with different porosity, measured total conductivity has been normalized by porosity using V.V. Skorohod's equation :

$$\sigma = \sigma_c(1 - 1.5P),$$

σ - conductivity of a porous body;

σ_c - conductivity of a compact body;

P - total porosity.

*Andrievskyi R.A. Introduction to powder metallurgy. Frunze: Ilim (1988) P. 174 (in Russian).

Conclusions

A lot of different studies focused on the development of new promising materials for SOFC application have been already done. Despite that, **zirconia-based materials remain the most common in use because they meet many requirements and have relatively low cost.**

Currently, **progress in development of SOFC is primarily concentrated on the development and implementation of new methods of SOFCs production to improve their structure and optimize properties of its components, rather than through the introduction of new materials.**

The next stage in the introduction of hydrogen energy and fuel cells in the economy of Ukraine should be the creation and testing of pilot technologies for production of SOFC combine heat and power (CHP) systems. Extensive demonstration activities should attract new investment in this field. The main attention should be focused primarily on the creation of pilot productions of stabilized zirconia powders and fuel cells from them and creation of SOFC-CHP systems prototypes.

Today, **there is an intellectual and raw material basis for the organization of high-tech production of power generation facilities based on SOFC in Ukraine**. Production and implementation of fuel cell technology in Ukraine can make a precedent for the "economic miracle" that took place in Germany, Japan and Korea due to high-tech productions.

Thank you very much for your kind attention!