RESEARCHES AND DEVELOPMENT OF A FUEL CELL WITH PROTONIC CONDUCTIVITY

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ABSTRACT

Technology and research results of single fuel cells (SFC) on the basis of $BaCe_{0,9}Nd_{0,1}O_{3-}\delta$ (BCN) electrolyte with the 78 % Ni + 22 % BCN anode and $La_{0,8}Sr_{0,2}MnO_3$ cathode, and also of experimental FC stack, assembled from six SFC, are stated.

INTRODUCTION

Development and perfection of high efficient and low emission energy sources on the basis of fuel cells, realizing a principle of direct electrochemical transformation of hydrocarbon natural fuel to electricity, is a dominant scientific and technical problem in power generation and has primary practical application.

Operation experience of power plants on the basis of various FC types (alkaline, phosphoric acid, molten carbonate) alongside with advantages demonstrates technical shortcomings, main of which is the presence of liquid components in FC systems. Therefore solid electrolytes on the basis of complex oxide compositions of rare earth metals have the doubtless prospect.

High efficient SOFC-based energy sources are possible, if SOFC materials with opportunities of fast ion transport, low power barriers for transition through "gas-electrolyte" interface and sufficient operational reliability could be developed. Alongside with common materials, such as stabilized zirconium dioxide (YSZ), alternative materials on the basis of cerates and , first of all, barium cerates (BC) are of significant interest for the researchers. The possibility of essential decrease of BC-based fuel cell operation temperature has predetermined outburst of interest to the development of SOFC with new electrolyte.

The work performed at the Russian Federal Nuclear Center under the contract with EPRI is devoted to the research and development of a fuel cell on a basis of $BaCe_{0,9}Nd_{0,1}O_{3-}\delta$.

The fragment of this work, covering SFC research, made under the scheme: 78%Ni + 22 % BCN / $BaCe_{0,9}Nd_{0,1}O_{3-}\delta$ / $La_{0,8}Sr_{0,2}MnO_3$, and also characterization of experimental FC stack, assembled from six SFC is reported.

TECHNOLOGY AND TECHNIQUE OF SFC RESEARCHES

The electrolyte membranes were made from powders of barium carbonate ($BaCO_3$), cerium dioxide (CeO_2) and one and a half neodymium oxide ($NdO_{1,5}$). The weighed components were mixed and rubbed with ethyl alchogol, and then dried at 150-200°C during 2 hours. To synthesize preliminary perovskite structure the obtained mixture was calcined in two steps at temperatures 900 and 1200 °C during 1 hour in platinum crucibles. Powder was dry milled after each calcination.

Then a powder was entered at hashing into 10 % solution of polyvinyl butyral in ethyl alcohol with dibutyl phthalate, solvent was removed and received paste was progressively rolled to reach required thickness. Membrane samples were cut out from green rolled sheets, which after initial annealing (500 °C) were sintered in air at 1490-1500°C during 2 hours. Thickness of received membranes was 0,5 mm.

Anodic paste consisting of 78% Ni + 22% BCN (19-23 mg/cm^2) was put on one side of a membrane and it was fired to electrolyte in air at 1350°C for 2 hours, and cathodic paste consisting of $La_{0,8}Sr_{0,2}MnO_3$ (76-94 mg/cm^2) was put on the other side and fired at 1250°C for 2 hours.

Then SFC was placed in a measuring unit and reduction of nickel oxide to metal on anodic coating was fulfiled. Characteristics were investigated at supply of humidified hydrogen to anode (consumption 5 l/hr), and humidified air - to cathode (consumption 24 l/hr).

RESULTS OF SFC RESEARCH

Voltage-current SFC characteristics in a temperature range 700-900°C are given in Fig.1 and have linear nature. The calculated ion transport numbers (t_i) vary from 0,9 at 900 °C to 0,94 at 700 °C. Current density at U = 700 mV and temperature 800 °C lays in the range 50-55 mA/cm^2.

SFC power as a function of current density is given in Fig.2. It can be seen, that I-P curves pass through a maximum. The maximum power increases with temperature growth and makes up 63-65 mW/cm^2 at 900 °C.

SFC ohmic losses at different temperatures are given in Fig.3.

It was not possible to measure anodic polarization with satisfactory accuracy. But we established, that maximum values of anodic overvoltage did not exceed 30mV. The main contribution to SFC polarization losses is due to cathodic overvoltage (Fig.4).

Researches of BCN electrolyte serviceability in various fuel mixes , containing 20, 30, 40 vol. % CO_2 in fuel cell: $H_2 + H_2O + CO_2$, Pt/BCN/Pt, air , were also carried out. In this case we used $BaCe_{0,9}Nd_{0,1}O_{3-}\delta$ membrane 1 mm thick. Porous platinum was used as electrodes. Working area of SFC was 1,54 cm^2. SFC total power as a function of fuel composition at 600-800 °C is represented in Fig.5. SFC electrical characteristics at long-term operation with pure humidified hydrogen, and with fuel mix, containing 20% CO_2 after 130 minutes of work, are shown in Fig.6.

The researches testify, that BCN-electrolyte with platinum electrodes keeps long-term serviceability in pure humidified hydrogen, but the CO_2 presence in fuel mix leads to irreversible deterioration of its electrochemical properties in a short interval of time. It result in a complex cell degradation: formation of barium carbonate in “electrolyte-electrode” interface, change of electrolyte structure, elamination of electrode coating.

Study of SFC electrical characteristics stability in time was carried out at temperature 905±6°C under the scheme: $H_2 + H_2O$, Ni + BCN/BCN/MLS, air. The resistance of an external load was chosen so that SFC gave out the maximum power. The electrical SFC characteristics (Fig.7) demonstrate stable work during 106 hours.

EXPERIMENTAL SFC STACK AND ITS CHARACTERISTICS

The doubtless interest in FC researches is the study of not only SFC behavior, but also, as the general purpose - research of SFC set, assembled in stack.

For realization of such researches the round BCN plates 26 mm in diameter and 1 mm thick were made by pressing (Fig.8). Electrodes (anode: 78 % Ni + 22% BCN, cathode: $La_{0,8}Sr_{0,2}MnO_3$) were put on and fired to plates surfaces. Platinum current collectors were fired by means of current-conducting glass to cathodic and anodic surfaces. SFC stack is a series of alternating anodic and cathodic gas cavities, separated by solid electrolyte. Channels for gas input and output are located perpendicularly to each other. SFC number in a stack is 6 pieces (Fig.9).

The SOFC stack is located in the ceramic frame with covers fixed in ceramic casing, in which supply of fuel and oxidizing gases to stack and removal from it are made (Fig.10).

The metal casing with SOFC stack is placed in the central part of electrical heater of the experimental block, the space between the stack frame and heater is filled with heat insulation (Fig.11, 12).

The researches were carried out with H_2 + 2,5 volume% H_2O as a fuel (consumption 4 l/hour) and with air as an oxidant (consumption 40 l/hour).

The individual characteristics of SFCs assembled in stack are represented in Fig.13, 14. Characteristics of FC stack are shown in Fig.15, 16.

Characteristics of FC stack, consisting of six connected in parallel SFC (total area 18,8 cm^2) at temperature 650 °C were received as follows:

open circuit voltage E= 0,866 V, maximum current I_{max} = 0,418 A,
current density J_{max} = 22,2 mA/cm^2 at U = 0,44 V,
maximum power P_{max} = 0,184 W, power density - 9,8 mW/cm^2.

CONCLUSION

Carried out researches of fabrication technologies and characteristics of FC on the basis of BCN-ceramics ($BaCe_{0,9}Nd_{0,1}O_{3-}\delta$) allowed to obtain additional scientific data, which testify the possibility of using investigated compositions in medium temperature solid oxide fuel cells with protonic conductivity, taking into account limited CO_2 content in a fuel gas.

ACKNOWLEDGEMENTS

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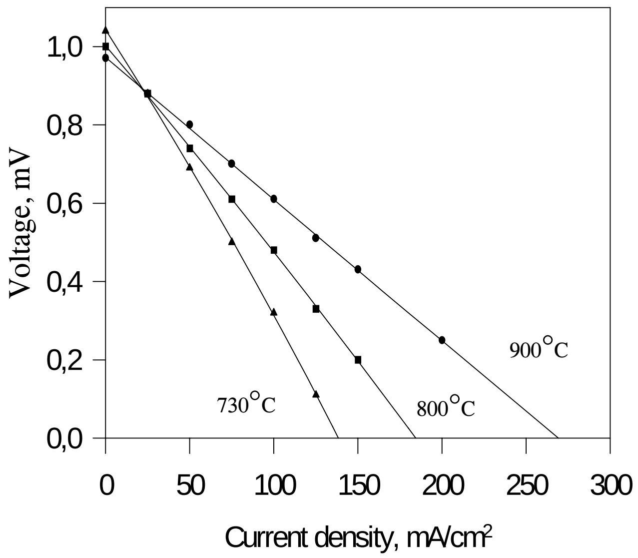

Fig. 1. SFC voltage-current characteristics

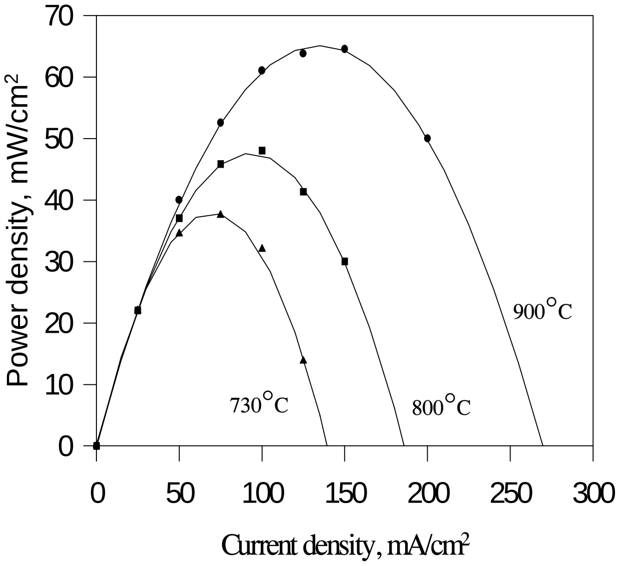

Fig 2. SFC power vs current Fig. density

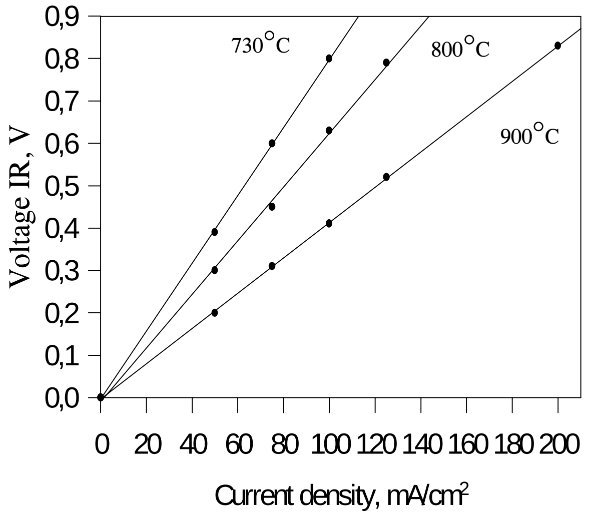

Fig. 3. SFC ohmic losses vs current density.

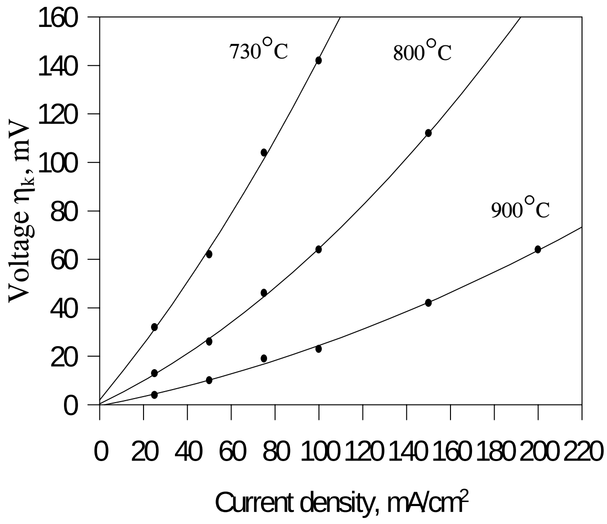

Fig. 4. SFC cathodic polarization.

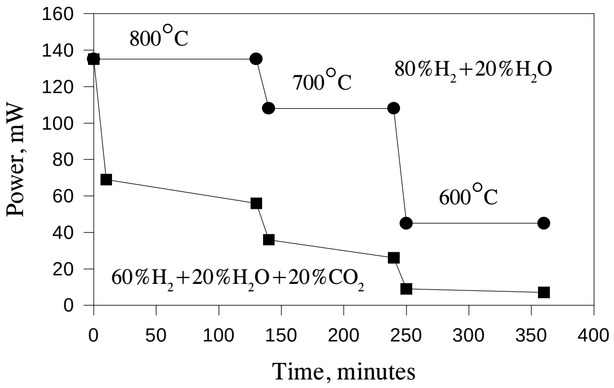

Fig. 5. SFC maximum power vs temperature and operation time in different fuel mixes

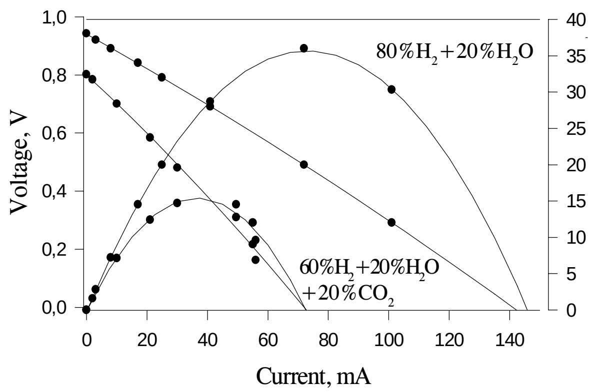

Fig. 6. Characteristics of SFC long-term operation with pure humidified hydrogen and with CO_2 - containing mix after 130 minutes operation

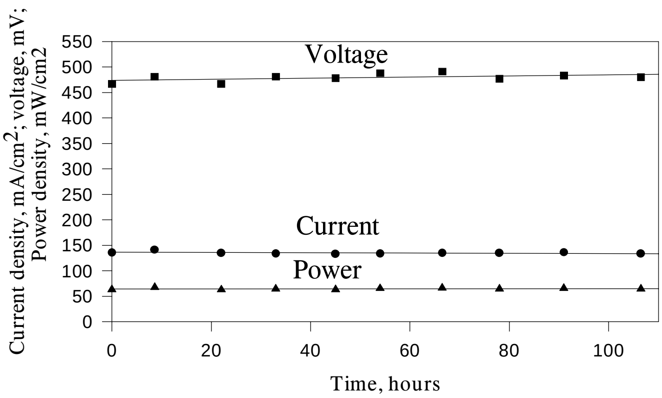

Fig. 7. SFC electrical characteristics vs. time

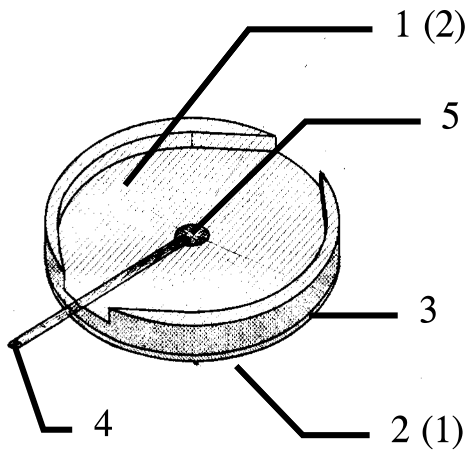

Fig. 8. SFC design
1 - anode, 2 - cathode, 3 - BCN -electrolyte,
4 - platinum current collector,
5 - current conducting glasses

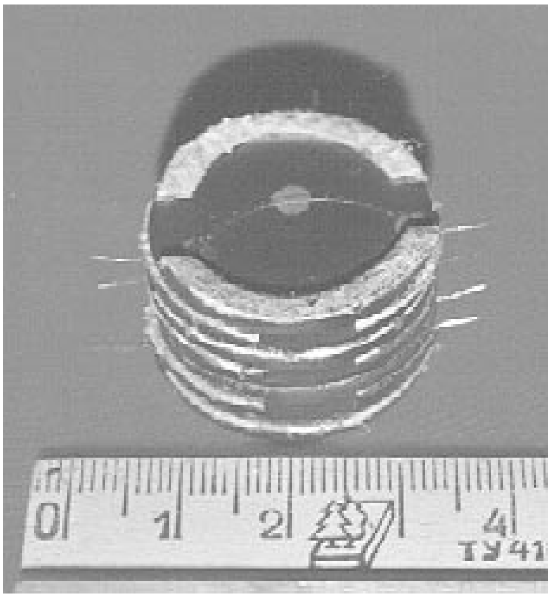

Fig. 9. Fuel cell stack

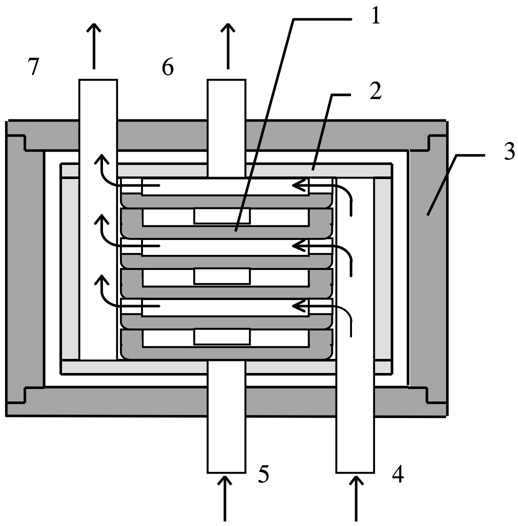

Fig. 10. Experimental stack design:
1 - SOFC stack, 2 - ceramic frame,
3 - heater frame, 4 - air,
5 - hydrogen, 6 - anode gas outlet,
7 - cathode gas outlet

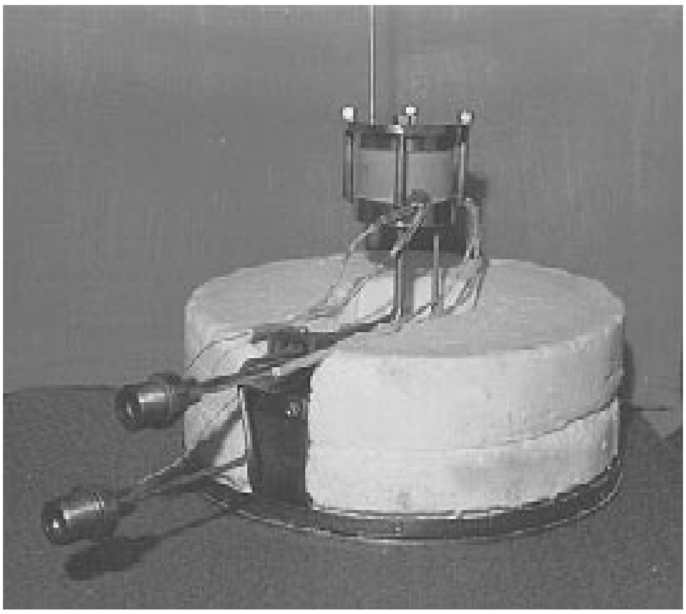

Fig. 11. Casing assembled with SOFC stack

Fig. 12. Experimental stack

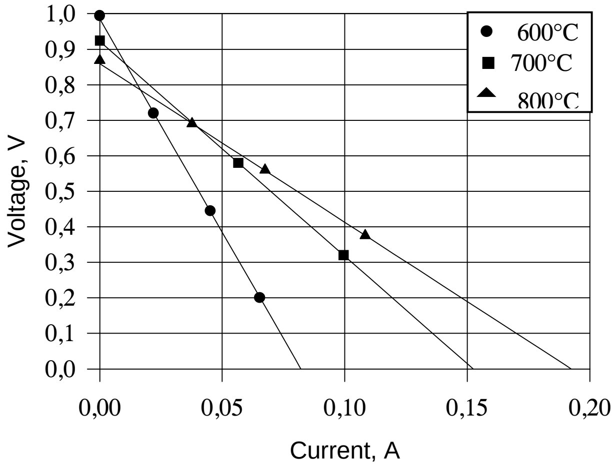

Fig. 13. SFC voltage-current characteristics

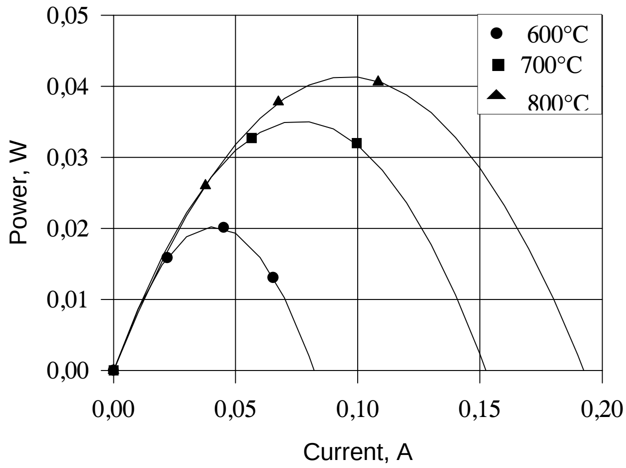

Fig. 14. SFC power vs. current

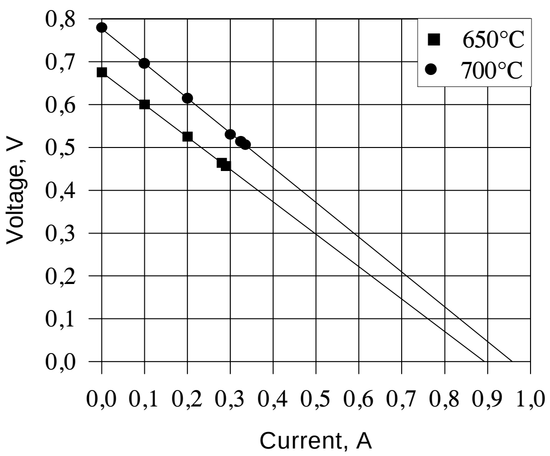

Fig. 15. SFC stack voltage vs. current

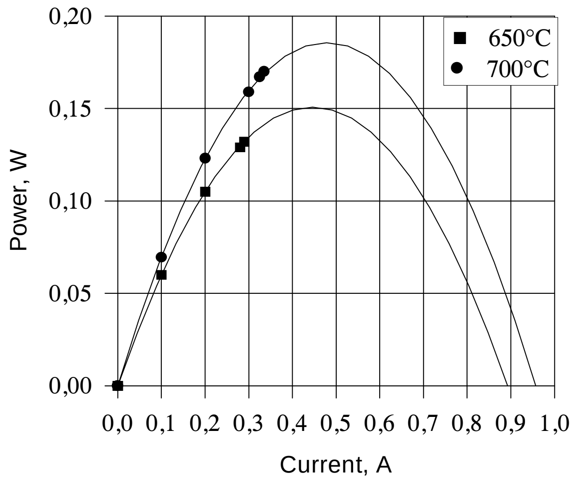

Fig. 15. SFC stack voltage vs. current