To summarize, the method of electric energy transfer considered in the present report may turn out to be beneficial in low-voltage transmission lines or in other cases where there exists unwanted extraneous electrical noise in transmission lines or circuit commutation devices. Furthermore, it can be employed when there is no way of applying metal conductors (for instance, in high-voltage devices) or when decreasing the weight characteristics of supply lines becomes a paramount requirement.

References

1. Basov N G, Krokhin O N *Fiz. Tverd. Tela* **5** 2384 (1963)
2. Bugge F et al. *Appl. Phys. Lett.* **79** 1965 (2001); Pikhtin N A et al. *Electron. Lett.* **40** 1413 (2004)
3. Broderick N G R et al. *Opt. Fiber Technol.* **5** 185 (1999)

PACS numbers: **82.45.–h**, 82.45.Yz, **82.47.–a**
DOI: 10.1070/PU2006v049n04ABEH005957

Portable fuel cells: their physics and micro- and nanotechnologies

A G Zabrodskii

1. Introduction

This report presents a brief review of the results of investigations carried out at the A F Ioffe Physical-Technical Institute (PTI) and at a number of other institutes of RAS in one of the branches of hydrogen power engineering, dealing with the development of portable fuel cells.

Actually, research in the field of energetics is a traditional topic for the Petersburg Physical-Technical Institute. It was here that Ioffe created the national scientific school of thermoelectricity and began the practical implementation of this effect for cooling. In the 1930s, nuclear studies were launched in a laboratory headed by I V Kurchatov with Ioffe's support. There the young scientists G N Flerov and K A Petrzhak discovered spontaneous uranium fission. At the beginning of the Great Patriotic War (1941 – 1945), Flerov was studying at a school for aircraft technicians, where he wrote his well-known letter to I V Stalin, in which he stressed the immediate need to begin work on the atomic bomb. This event marked the beginning of the Soviet Atomic Project and the birth of the nuclear power industry, to which the researchers at PTI contributed greatly. It was at PTI that V N Tuchkevich as a scientific leader and his colleagues developed a new area of research — high-current semiconductor electronics. Studies in highly effective solar power engineering based on the use of semiconductor heterostructures may be highlighted as an outgrowth of the backbone area of research in physics, engineering, and technology developed at PTI by Zh I Alferov and the scientific school he created in the field of semiconductor heterostructures. For more than half a century, the PTI staff has participated in physics research programs, in developing technologies associated with controlled fusion based on tokamaks, and in the diagnostics of hot plasma. Several years ago, an entirely new spherical tokamak 'Globus-M' became operational at PTI and physical investigations began on it.

Relatively recently, PTI became actively involved in hydrogen power research within the program that incorporated RAS and the Norilsk Nickel Mining and Smelting Co. (later the program gave birth to the National Innovation 'New Energy Projects' Company). Here I will speak only of works dealing with the development of new types of portable fuel cells. The material I will present illustrates the typical approach to research at PTI: from scientific investigations to basic technologies and later to the development of new facilities. The basic technologies in this field are those involving the deposition of monodispersed nanocatalysts (Section 3) and also silicon micro- and nanotechnologies (Section 4) utilized to develop portable fuel cells (Section 5). I will also discuss possible ways of raising the efficiency and specific power of fuel cells (Section 5). Minimum information about hydrogen energetics and fuel cells is given below in Section 2.

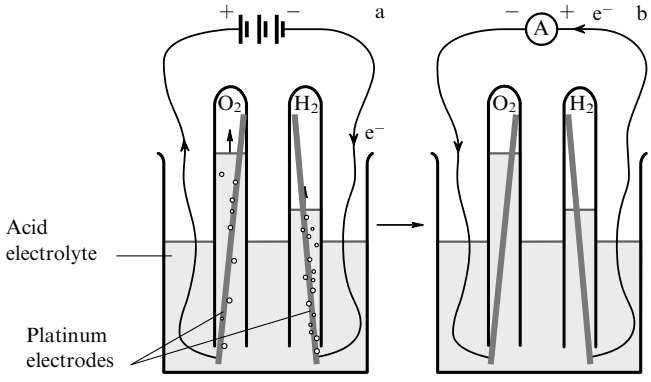

Figure 1. An electrochemical cell operating in the electrolysis mode (a), and in the fuel-cell mode (b).

2. Hydrogen power engineering and fuel cells

The interest in generating power through the use of hydrogen is stimulated by the gradual depletion of fossil fuel reserves [1] and by ecological problems, as well as by the need to raise the efficiency of energy conversion.

What makes hydrogen so attractive as an energy carrier is, on the one hand, the great variety of sources for its production, among which are coal, natural gas, biomass, solar energetics, thermal energetics, photoelectric power engineering, hydroelectric power engineering, wind energy, nuclear electrical power engineering (the last four via electrolysis), and nuclear thermal power engineering. On the other hand, the merits of hydrogen manifest themselves most vividly when it is used as an energy carrier in key devices of hydrogen power engineering, namely, fuel cells of various types, which encompass a broad spectrum of power outputs: from several dozen milliwatts to several megawatts.

The first fuel cell was developed by William R Grove of Great Britain in 1839 already. His device produced electric current from hydrogen and oxygen reacting at platinum electrodes (Fig. 1 [1]). When an external source of electricity

[1] Note that our ideas about the depletion of oil reserves are basically formed by the rising prices for crude oil and petrol. These prices strongly depend on inflation of world currency and political stability in the main regions of oil production. A sharp increase in oil prices usually accompanies political upheavals and wars in such regions. The absolute record in oil prices with inflation taken into account was not reached in recent years but on the verge of 1970s and 1980s when the Iranian Revolution took place. Nevertheless, the very fact of substantial depletion of reserves of natural fuel, primarily crude oil, is indeed true and is certainly a troubling problem for the oil (and gas)-importing countries.

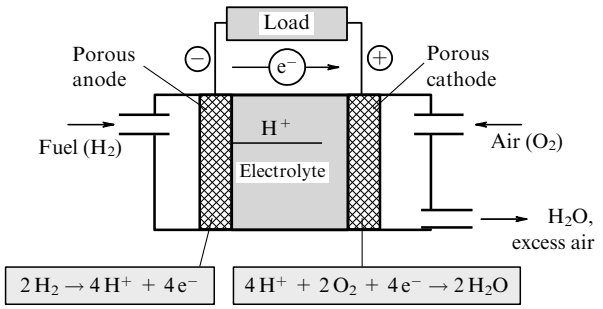

Figure 2. Schematic diagram showing the operation of a fuel cell.

was attached to this electrochemical cell, the cell could operate in the electrolysis mode. When the external circuit was closed, it experienced a current flow and the electrochemical cell operated in the fuel-cell mode.

Grove was also the first to find that the efficiency of the fuel cell is determined by a 'bottleneck' — the boundary of three phases (gaseous fuel, electrolyte, and electrode), to carefully examine new ways of raising the efficiency of electrolytes and electrodes, and to appraise the importance of hydrogen as an alternative to wood and coal.

Figure 2 schematically shows the operation of a planar fuel cell together with the main electrochemical reactions in the anode and cathode parts. It was found that the reaction rate increases with temperature and the effective surface area of the electrodes, and also increases if a catalyst is utilized (not shown in Fig. 2, but usually located at the electrode–electrolyte boundary; see Fig. 6). Note that at present solid electrolytes are being widely used in fuel cells, namely, fuel cells with a solid-polymer membrane, and solid-oxide fuel cells. The main requirement that such electrolytes must meet is a high proton or ion conductivity but low electron conductivity.

The main merits of fuel cells are as follows:

(a) a potentially high efficiency η, since at room temperature

$$\eta_{\max} = \frac{\Delta G}{\Delta H} = 91\%, \qquad H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O,$$

$$\Delta H = -242 \text{ kJ mol}^{-1}$$

(combustion process: formation enthalpy $U + pV$),

$$\Delta G = -220 \text{ kJ mol}^{-1}$$

(generated electric energy: Gibbs energy $U - TS$);

(b) the possibility of utilizing fuels with high energy content (hydrogen and hydrocarbons with a specific energy capacity several dozen times greater than that of Li-ion batteries);

(c) an ecologically clean sources of energy, and

(d) the absence of moving parts and noiselessness (for portable fuel cells).

It is important to keep in mind that fuel cells can use, in addition to hydrogen, other gaseous (biogas, natural gas, etc.) or liquid (methanol, ethanol, etc.) fuels. Fuel cells are usually divided into three large groups according to the areas of application: stationary, for use in vehicles, and for home appliances and electronic devices.

Table 1 gives a rough idea of the characteristic parameters of fuel cells entering the third group, what is known as portable fuel cells, which are used in power sources for

Table 1.

Areas of application	Mobile phones	Laptops
Dimensions, cm	2–5	5–20
Power output, W	~ 0.1	10–20
Power capacity, W h	1–5	40 –150
Main types	Methanol, air-hydrogen	Methanol, air-hydrogen

mobile phones and notebooks. The market interest in portable fuel cells is, understandably, caused by the growing sales of portable electronic devices. In this report I will touch on the topic of most compact and miniature portable fuel cells. Usually, the electrolyte in such fuel cells is a solid-polymer membrane. Porous carbon or silicon materials are employed as a base for the development of electrodes. Actually, this constituted the entire input data at the beginning of our research. Our approach consisted in using the existing technologies of microelectronics and microelectromechanics for producing porous silicon electrode structures, as well as in applying a technology, developed at PTI for producing monodispersed nanomaterials by laser electrodispersion, to the deposition of catalytic coatings. Parallel to these developments, the problems of fabricating a silicon-based hydrogen-separating membrane and 'extending' the reaction zone by using a currently developed material with mixed electron–proton conductivity were also investigated.

3. The technology of depositing monodispersed nanocatalysts

As is known, the large consumption of platinum in the catalysts of modern fuel cells (at a level of approximately 1 g kW^{-1}) will sooner or later limit the development of hydrogen power engineering. It has therefore become extremely important to formulate and solve the problem of developing a highly effective catalyst with fairly small platinum consumption.

To this end, we used an original laser nanodispersion technique [2], which is a laser ablation, accompanied by the process of self-organizing division of droplets of a target (Fig. 3 gives an idea of the method by which a monodispersed nanocatalyst is formed).

The parameters of the laser beam (1.06 μm, 1 GW cm^{-2}, 25 ns) were selected so as to initiate a cascade division of

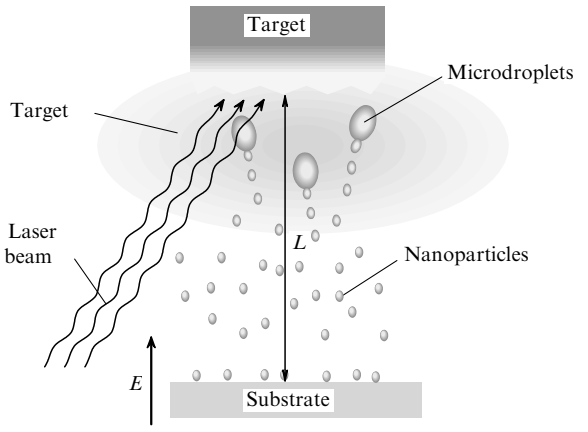

Figure 3. Fabricating a monodispersed catalyst.

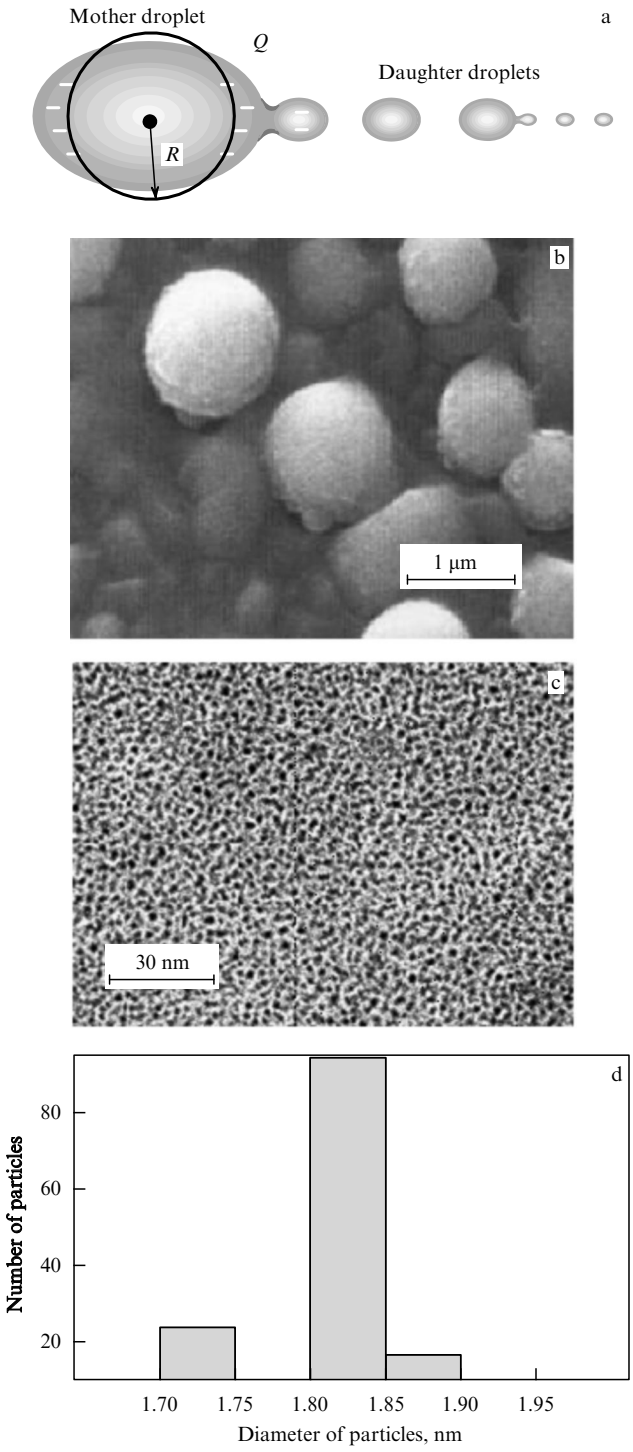

Figure 4. (a) Division of charged droplets in plasma. (b) Daughter droplets on a substrate located near the target ($L = 0.5$ cm). (c) Distribution of nanoparticles over the surface of the substrate located far from the target ($L = 5$ cm). (d) Nanoparticle-size distribution.

submicrometer-sized droplets spattered from the target. A nonuniform electric field (~ 1 kV cm^{-1}) collected the nanoparticles onto the substrate and separated them.

The physical basis of the method resides in the Rayleigh instability of charged droplets in plasma, which leads to their cascade division. The related problem was examined, for instance, in Ref. [3]. An initially stable spherical droplet of radius R becomes unstable in relation to fission if the charge Q it acquires in the plasma exceeds a critical value Q_{cr} specified by the relationship

$$Q > Q_{cr} = 8\pi(\varepsilon_0 \alpha R^3)^{1/2}, \quad (1)$$

where α is the surface tension coefficient of the liquid.

Experiments carried out at PTI showed that the intuitive idea that a droplet divides into two roughly equal parts is unrealistic: one of the daughter droplets proves to be much smaller than the other, which accelerates the disintegration process. This type of droplet division is shown in Fig. 4a. The process was verified through experiments in which droplets were deposited on a substrate located near the target. The geometry of this experiment corresponds to Fig. 4b, where the seeds of small daughter droplets are clearly visible on some of the mother droplets.

If the electron temperature of the plasma in the laser torch exceeds 30 eV, droplets of all sizes prove to be unstable in relation to division. Figure 4a illustrates this fact.

Nevertheless, cascade division finally stops because of a rapid increase in the emission of electrons from the droplets and the rapid discharging of droplets as the size d of the daughter droplets decreases to a certain minimum value. As shown in Ref. [4], this parameter equals

$$d_{min} \approx 8 \times 10^{-7}\, \varepsilon \alpha^{-3}, \quad (2)$$

where ε is the work function.

In particular, d_{min} for platinum amounts to about 2 nm (Fig. 4c) at a minimum dispersion of the particle diameter (Fig. 4d). It is important that precisely this size proved to be optimal for the effective operation of catalytic coatings.

For instance, most of the platinum nanoparticles produced by this method have the same size $d = 1.8$ nm. In view of the high cooling rate $dT/dt > 10^7$ K s^{-1}, the particles are amorphous and do not coagulate. This technology allows depositing on the fuel-cell units carefully metered layers (and parts of layers) of monodispersed particles of highly active catalysts (not only platinum) with sizes ranging from 2 to 3 nm, and thus appreciably reduces the consumption of materials of the platinum group to approximately 0.1 g kW^{-1}.

4. Fabricating electrode structures from macroporous silicon. Formation of electrodes with a 10-nm membrane for purifying hydrogen

The employment of technologies for fabricating porous silicon[2] solves the problem of moving to micro- and nanotechnologies needed for the miniaturization of the components of portable fuel cells. The microstructurization of silicon opens the possibility of fabricating

- channels for supplying fuel and oxidizer and removing the reaction products;
- porous electrodes (anodes and cathodes) with a well-developed active surface which can be utilized for depositing catalysts, and
- radiators for heat removal.

The use of technologies worked out in modern silicon electronics and microelectromechanics helped in developing ways of fabricating multifunction electrode structures from porous silicon. Electrodes fabricated from such structures

[2] Initially, the development of these technologies at PTI was related to other problems (in particular, problems related to the use of what is known as photon crystals).

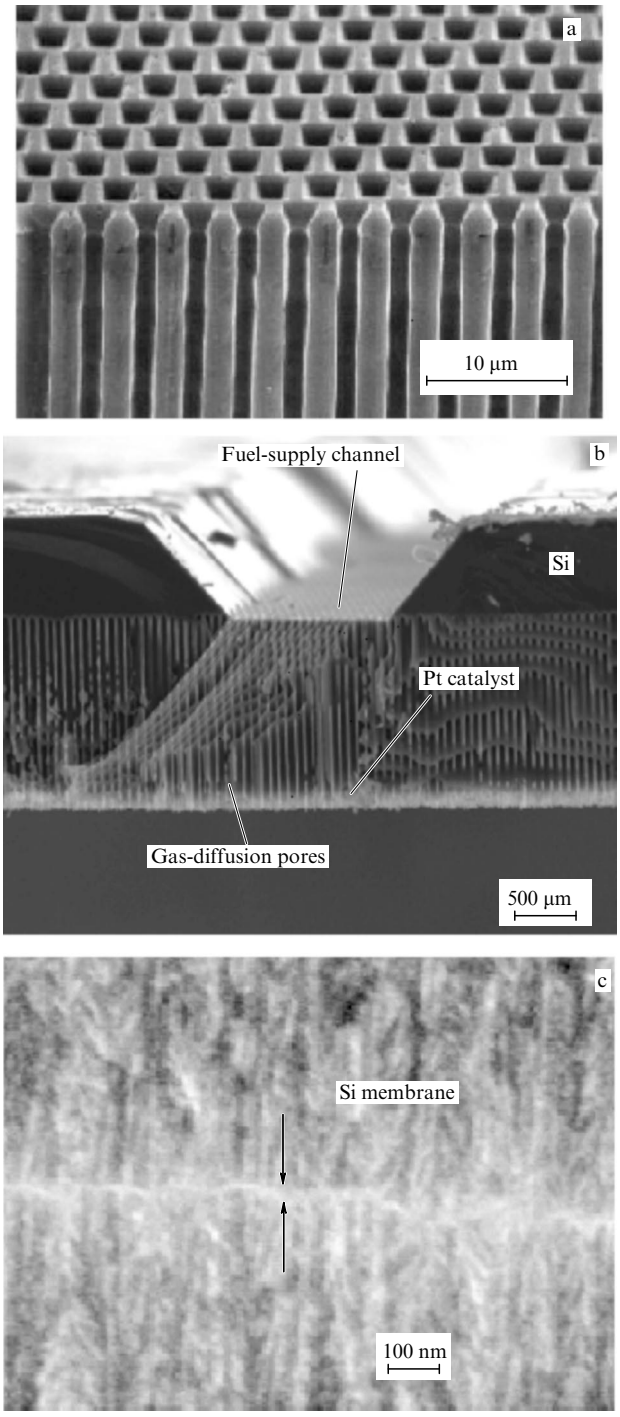

Figure 5. (a) Regular channel electrode structure of macroporous silicon. (b) Cross section of the anode part of a fuel cell. (c) Micrograph of the cross section of a 10-nm silicon membrane, taken with the help of a transmission electron microscope. Channels with a diameter of about 20 nm are located above and below the membrane.

with pore sizes ranging from 1 to 100 μm [3] substantially reduce the size of fuel elements and guarantee the required specific efficiency.

As an illustration, Fig. 5a presents a micrograph of a regular channel structure of an electrode fabricated from macroporous silicon by photoelectrochemical etching [5]. By using a simplified version of this technology it is possible to fabricate irregular channel structures with a random distribution of the channels on the basis of the self-organizing effect without employing masks.

[3] Such materials are known as 'macroporous'.

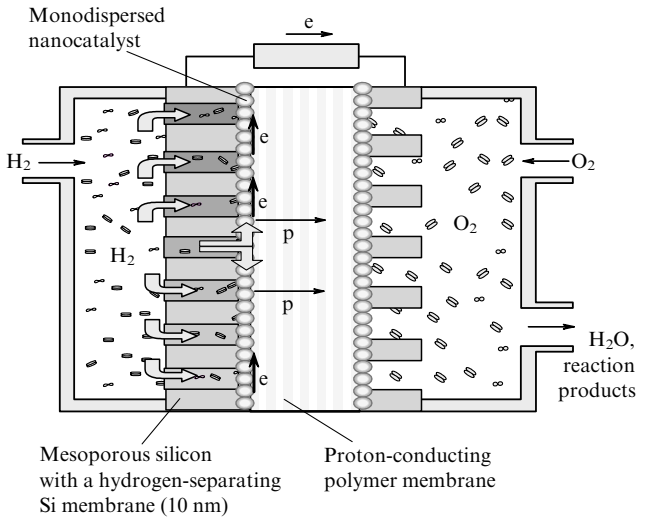

Figure 6. The design of a portable fuel cell that is being developed.

Figure 5b depicts the cross section of a multifunction monolithic anode of a methanol fuel cell fabricated from macroporous silicon at the Institute for Microelectronics Technology, RAS in Chernogolovka [6].

To solve the problems associated with the formation of porous electrodes and the purification of hydrogen, a new method has been developed to fabricate electrodes with a 10-nm hydrogen-separating silicon membrane, which effectively operate at room temperature (Fig. 5c). The method is based on a technology elaborated at PTI for fabricating mesoporous silicon (the pore diameter amounts to 20 nm) by two-sided anodic etching.

5. The use of mature technologies in manufacturing portable fuel cells. A way of increasing the efficiency and specific power output of fuel cells

The technologies I have described above have been applied to developing portable fuel cells of various designs [7]. Figure 6 gives an idea of the design of such a cell with a proton-conducting polymer membrane, in which a monodispersed nanocatalyst was deposited on an electrode structure fabricated from mesoporous silicon with a hydrogen-separating 10-nm Si membrane.

In order to increase the reaction zone of fuel cells, interfacial composite layers based on polymers and carbon nanotubes have been developed at PTI and the Institute of High-Molecular Compounds of RAS [8]. The structure of such layers which possess mixed electron – proton conductivity is shown in Fig. 7. Their utilization in electrode structures suggests that the reaction zone will get 'extended', which will raise the efficiency of fuel cells.

6. Conclusion

In this report I have not mentioned the problems associated with the development of portable fuel cells that lie outside the scope of my topic, i.e., fuel cells that are not grounded on micro- or nanotechnologies, but nevertheless were subjects of our investigations. Among them is the problem of optimizing

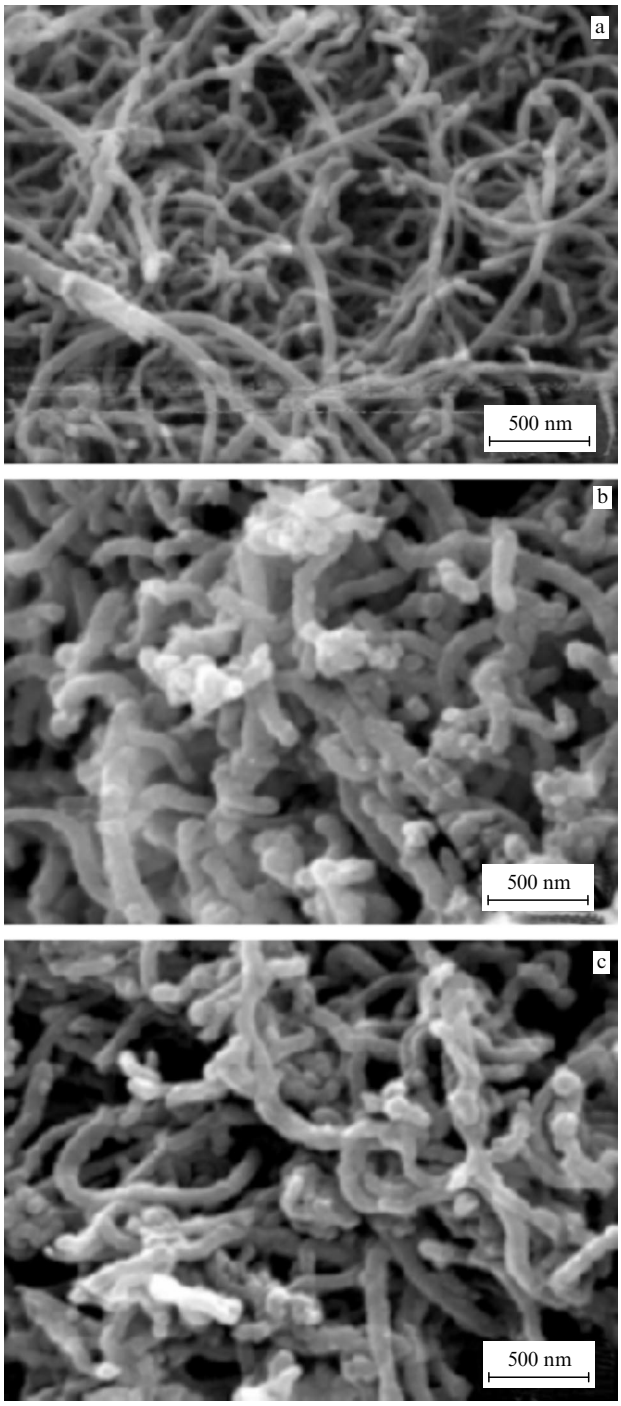

Figure 7. Original carbon nanotubes (a); nanotubes covered with polyaniline (b and c) with 70 and 90 wt.% of polyaniline, respectively.

the fuel for these cells. Due to its high energy content, the most widely used fuel for portable solid-polymer fuel cells — methanol — has many essential drawbacks, which forces researchers to look for substitutes [9].

Among the most important difficulties in developing new fuel cells is the problem of matching their elements that are fabricated in different technological processes, say, matching the solid-polymer membrane with electrodes fabricated from a porous inorganic material.

Nevertheless, all research, including the development of our basic micro- and nanotechnologies described in this report, some of which are already among the best in the world,[4] suggests that the problem of developing efficient portable fuel cells on the whole will be solved.

References

1. Larminie J, Dicks A *Fuel Cell Systems Explained* 2nd ed. (Chichester, WS: J. Wiley, 2003)
2. Kozhevin V M et al. *Dokl. Ross. Akad. Nauk* **387** 785 (2002) [*Dokl. Phys. Chem.* **387** 324 (2002)]
3. Landau L D, Lifshitz E M *Elektrodinamika Sploshnykh Sred* (Electrodynamics of Continuous Media) (Moscow: Gostekhizdat, 1957) [Translated into English (Oxford: Pergamon Press, 1960)]
4. Kozhevin V M et al. *J. Vac. Sci. Technol. B* **18** 1402 (2000)
5. Astrova E V et al. *J. Micromech. Microeng.* **14** 1022 (2004)
6. Vyatkin A et al. *J. Electrochem. Soc.* **149** G70 (2002)
7. Astrova E V et al., in *Mezhdunar. Forum "Vodorodnye Tekhnologii dlya Proizvodstva Energii", Moskva, 2005* (Intern. Forum "Hydrogen Technologies in Energy Production", Moscow, 2005) Abstracts (Moscow, 2006) p. 188
8. Kompan M E, Sapurina I Yu, Stejskal J, in *I Rossiiskaya Konf. po Fizicheskim Problemam Vodorodnoi Energetiki, Sankt-Peterburg, 2004* (1st Russian Conf. on Physical Problems in Hydrogen Power Engineering, St.-Petersburg, 2004) Abstracts (St.-Petersburg, 2004) p. 23
9. Goryachev D N, Malyshkin V G, Zabrodskii A G, in *Mezhdunar. Forum "Vodorodnye Tekhnologii dlya Proizvodstva Energii", Moskva, 2005* (Intern. Forum "Hydrogen Technologies in Energy Production", Moscow, 2005) Abstracts (Moscow, 2006) p. 147

PACS numbers: **28.70.+y**, **47.40.–x**, **62.50.+p**
DOI: 10.1070/PU2006v049n04ABEH005958

Physics research during nuclear explosions

E N Avrorin, V A Simonenko, L I Shibarshov

1. Introduction

Possibly no other engineering or technical endeavors of humankind have involved as much science as nuclear explosives have. The development of atomic and hydrogen bombs has required integrating knowledge from a wide circle of scientific fields and demanded huge technical and material resources — while, on the other hand, stimulating research into physical processes occurring under conditions beyond the reach of laboratory experiments.

Nuclear explosions produce pressures of up to several billion atmospheres and temperatures of up to hundreds of millions of degrees; they emit intense radiation — electromagnetic waves ranging from radio waves to hard gamma rays, and neutron fluxes in the energy range from fractions of an electron-volt to dozens of megaelectron-volts, and they involve a variety of physical processes, including shock and detonation waves, cumulation, turbulence, phase transformations, radiative energy transfer, dissociation and ionization, as well as fission and fusion nuclear reactions.

Given all this, nuclear explosions offer a unique set of fundamental and applied research opportunities — some of which unfortunately have been left unaddressed.

Listed below are research areas where much effort has been spent and good progress made.

(1) Thermodynamic properties of substances, equations of state, and phase transformations.

[4] For instance, the results achieved in research on monodispersed catalysts seem to be unique.