Innovative Approach

SOLID PROTONIC CONDUCTORS: CONDUCTIVITY, STRUCTURE, PROTON TRAPS, PHASE TRANSITIONS, EXCESS HEAT AND NEUTRON ANTI-EFFECT

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Abstract
In our study of high temperature proton conductor (HTPC) it is shown that thermal and radiation effects can be correlated to a set of peculiarities of their structural and electric properties. These materials may be considered as model object to be searched for the elucidation of mechanism of anomalous phenomena in solid/deuterium systems. The ceramics are in specific cases superior to palladium. Our experiments were conducted with ceramic sandwich-like structure on the base of strontium cerate, espesially synthesized, with porous platinum or palladium coating. Analysis of some peculiarities of conductivity nature of HTPC shows that conductivity can not be satisfactorily explained without considering interaction between protons as well as protons and crystal lattice environment. The available electrochemical data on ionic (in this case on hydrogen nuclei) transport suggest that processes of nuclear interaction simultaneously occur which may result in cold fusion phenomena. The phase transition at 445°C and similar behavior at other points in the range to 1000°C were found. We have established that pass through a region of phase transition is correlated to heat effect. A transition from exothermic to endothermic effect during cooling and heating of ceramic has been found. Analysis of X-ray studies shows that processes of explosive character inside lattice of sample, which give rise to the neutron and heat effects, can occur. We observed a incomprehensible influence of background on neutron emission, as well as a decay of neutron background inside the protection container with the sample.

1. Introduction

This study is the continuation of the investigation of anomalous phenomena in high temperature protonic conductors (HTPC) / deuterium systems, which have been submitted to the 3-th, 4-th and 5-th International Conferences on Cold Fusion. We reported about both discovered excess heat and neutron generation effects in such systems, and new physical properties of protonic conductors (e.g. the reduction of the ceramics at some conditions or the availability of unknown phase transition in samples, based on $Sr(Ba)CeO_3$, in the neighbourhood of 450°C), connected with manifestation of those effects. This suggests that the HTPC offer the greatest promise for cold fusion investigations.

In [1-4] the observations of excess heat and neutron emission in solid protonic conductors such as bronzes and $ACedO_3$ ceramics (where A is Sr or Ba, d is dopant, such as Nd, Dy Yb etc.) have been reported. In [5] the appearance of radioactive isotopes in the ceramics has been announced. In particular, as perspective materials for investigation of anomalous phenomena the different HTPC - Pd and HTPC - Pt sandwichs were used.

In [2] we proposed the hypothesis about the vital role of conductivity nature for such anomalous behavior. Furtheover, many cold fusion effects in solids can be considered with universal viewpoint based on proton conduction. In [2, 4] we found some examples of correlations of excess heat and conduction properties in doped $SrCeO_3$ ($BaCeO_3$) - Pt(Pd) systems.

This paper reports the subsequent investigation of possible correlation between anomalous effects in proton conductors and their electrical and structure properties.

2. Methods, results and discussion

Neutron measurements

The samples were prepared from protonic conductors based on the doped $SrCeO_3$ or $BaCeO_3$, with Pt or Pd porous electrode covers, in the form of discs as that is described in [4] .

The principal neutron registration system consists of two thermal neutron detector rings, with 15 counters in each ring, placed in a paraffin moderator (see fig.1 in ref. [4]). The plant well is of diameter 200 mm, the external ring is 350 mm in diameter, the internal ring is 250 mm in diameter. The cell with ceramic sample is installed in the well. The registration system is placed in a radiation shielding box, which consistes of polyethylene bricks contained 3 percent of boron.

The nuclear electronics simultaneously allows the displaying of amplitude distribution of events registered as result of nuclear reaction with boron nuclei in the counters, and time information on the neutron detector signals appearing, as well as result distribution of time intervals between events, successively registered both the neutron detector rings and the additional flat neutron detector placed on top of the box, within 1 ms. The signals from each detector system have been amplified by the preamplifier. The signal was sent to the spectrometric amplifier with shaping time constant 2mks, then it was treated by the analog-to-digital converters with conversion time less than 4 mks. A pulse amplitude code and pulse time mark have been written into intermediate memory by help of the synchronizator. The information was stored by means of CAMAC in PC-486 for further analysis, based on the methods developed in Los Alomos [6] and Dubna JINR [7] . The principal analysis involves the fitting of time distributions obtained in effective and background exposures.

To determine the efficiency of the detector ring a calibration with a Pu-α-Be neutron source (12000 ± 2500 n/s intensity into 4π angle) was made. The efficienty of the ring measurement was 1.5 ± 0.4 percent with a certain type of used counters. The measurement of the background by this system without voltage on the sample during two day was shown counts rate to be 0.08 1/s. It was established that for reliable analysis it is necessary to consider pulses in the range from 31 to 128 channels in the amplitude distribution, the rest part may be connected with detectore noise, electronic hindrance, electric and acoustic signals.

The experiments were described in references [4, 8]. In a serie of experiments during cooling the solid electrolytes to room temperature, after its electrolysis in deuterium atmosphere and thermal treatment by cooling-heating, the pulse count rate was observed as follows:

Pulse time, mks	Channel Number	Pulse time, mks	Channel Number
3 032 804	73	12 104 138	36
4 305 050	49	12 104 218	110
12 104 026	42	12 669 726	158
12 104 052	28	12 923 576	119
12 104 076	83	12 923 768	>255
12 104 098	28	12 957 710	160
12 104 114	33	12 975 742	>255

Pulse time, mks	Channel Number	Pulse time, mks	Channel Number
13 407 850	163	13 836 316	>255
13 407 884	>255	14 381 008	233
13 836 264	195		

The analysis of amplitude spectrum and time distribution of the events does not permit to make unambiguous conclusion about the nature of the observed burst. It may be in principe explained as: i) "sly" electrical hindrance, ii) neutron burst, in which time interval between the acts of neutron registrations may be less than 20 mks. The second explication is fully justified. The observed value of pulse count was insignificant greater than background level. The maximum background value, obtained after a number of measurements, has been shown as 9 pulses for measurement period of 16.8s. The "successful" obtained pulse count time distribution in the mentioned experiment in the time interval was fixed as 21 events.

Excess heat measurements

The method was described in [4]. Nontheless, basic information will be replicated below. As calorimeter the metall (Al) cylinder was used for the most part, and in some cases we conducted the excess heat measurements with the use of Calvet-type microcalorimeter.

We used a inner heater, placed in metallic cylinder, for two purposes: 1) for calibrating the calorimeter, 2) for creating strongly non-equilibrium conditions which manifest itself in the formation of temperature gradient at the sample.

The power was determined with the calibrating curves found for direct (U=10 V) and reverse pulse load (U=10 V or 40 V) of electrolysis of solid electrolytes under hydrogen/deuterium atmosphere at high temperature. This investigation has been conducted with particular reference to the pass through temperature region of phase transition in the cerate samples. The heat power given out during electrolysis in the case of reverse current can not be directly detected by this method without a special updating. That is why, the electrolysis power was calculated in line with maximum current.

The results of our large body of research are typical for the results presented at ICCF-5. Little doubt can be that a unknown heat excess effects exist, but their nature to be investigated. The heat excess exceeds power spent to producing electrolytic processes over 10 - 1000 percent depending on way of loading by deuterium. The thermal effect was greater for reverse current than for direct current, it was less for hydrogen atmosphere than for deuterium one.

The microcalorimetric investigations showed that both processes of output of heat pulses and decay of heat at such electrolysis take place. We found some regions in the temperature range from 250°C to 800°C connected with abnormal heat spike like behavior clearly defined for these doped ceramics, in particular near 500°C and 630°C (see typical curve 4 in [4]). The voltage of 10 V was applied to the sample. During the cooling of the sample we observed enough noticeable summary endothermic effect, while during heating of the ceramic, inversely, the exothermic effect has been found, both for hydrogen and deuterium atmosphere (greater for deuterium). This may indicate phase transition or other unknown process in the ceramic lattice. It should to note that in the period after our presentation at ICCF-5 the similar spike heat liberation and heat decay have been observed in clean barium cerate [13]. In contrast to that experiment we found this effect in doped ceramic. It is essential since the proton conduction exist precisely in doped samples of such composition resulted in a manifestation of cold fusion phenomenon.

As to nuclear products, the most likely exess heat is not correlated with neutron emission. But the mechanism of heat effect remains unclarified. In hydrogene atmosphere the exceeding of neutron background was not observed. This probleme has aroused considerable interest in connection with investigation of phase transitions in HTPC, as it will be discussed below.

Conductivity

The experimental studies of conduction of electrolytes such as $SrCeO_3$ or $BaCeO_3$-based doped ceramics are summarized as follows [2, 4, 9, 10] : i) these oxides have p-type conduction in atmosphere free from hydrogen, ii) in hydrogen atmosphere they exhibit pure protonic conduction at temperature of 500° - 900°C, the conductivity is of 0.001 - 0.01 S/cm, iii) the protons are formed as results of processes:

$$H_2O + V_0'' \Leftrightarrow O_0^{\times} + 2H^{\bullet} \qquad (1)$$

$$V_0'' + 1/2O_2 \Leftrightarrow 2h^{\bullet} + O_0^{\times} \qquad (2)$$

$$H_2O + 2h^{\bullet} \Leftrightarrow 2H^{\bullet} + 1/2O_2 \qquad (3)$$

$$H_2 + 2h^{\bullet} \Leftrightarrow 2H^{\bullet} \qquad (4),$$

when V_0'' - oxygen vacancies, $O_0^{\times}$- oxide ion in the lattice, $h^{\bullet}$- hole, $H^{\bullet}$- proton, iV) in relation to gas pressure the reduction of sample may occurs resulted in the appearence of n-type electronic conduction.

It was been established that these conditions are sensible for manifestation of anomalous phenomena in ceramic-deuterium systems. The electrochemical observations are the most important for elucidation of the mechanism of cold fusion processes, which evidence that the nature of conduction can not be explained without idea of interactions of protons with lattice environment. The process of proton hops in the lattice formed the conductivity mechanism, is unknown in details. The appreciable energy-charge transfer processes may take place. It follows that conditions for nuclear interactions into ceramics can be realised resulting in so-colled cold fusion. This question will be described more thoroughly in the other papers.

Structure and structure changes

This problem is more complex in character than it seems. We conducted the analysis of X-ray structure data both pre- and after experiment with the samples by DRON-3 diffractometer. Our X-ray study shows that the sample based on $SrCeO_3$ has the orthorombic structure. However the structure can be strongly distinct even with identical composition depending from preparation of sample [13]. The chemical purity of ceramics, its microstructure pecullarities, its thermal history could favor one or the other of the possible conductivity mechanisms [14]. Some indications exist that the structural modifications of the lattice can take place during thermocycling when phase transitions are also considered. This can drastically affected the deuteron distribution, the splitting of the deuteron positions and their migration. We observed also the production of the additional phases such as $SrCO_3$ and CeO_2 in the test specimens, and the oscillations of electrical charasteristics . This can have a direct influence with non-reproducibility of cold fusion results.

The latest our investigations show that the samples, used to advantage in experiments on heat and neutron detection, have sever structural changes, which give an insight into mechanism of processes. A sharp decrease of the volume of elementary cell of the sample generating heat pulse has been found by X-ray method. As an example, the SrCeO3-based ceramic characterized by excess heat has in value V=314,9± 0,1 Å^3 before the beginning of experiment, and V=313,8± 0,1 Å^3 [11]. For oxide sodium tungsten bronzes resulted in neutron burst, this decreasing is more evident. All the crystals for which neutron emission was not observed, have the volume of the elementary cell enlarged or not changed [12,15]. From these results logical deductions are drawn that the process of compression happens in the lattice. In this connection it is well to bear in mind that the test conditions with ceramics (electrolysis voltage U < 100 V, reverse current frequence f is of several of Hz or of a fraction of Hz) are similar to conditions of P.Bridgman's reological explosion under pulse electrical loading of materials. It is common knowledge that in conditions of Bridgman's explosion the many of chemical and physical processes in solid can go through the other mechanism as compared with normal conditions. This point will be corrected in a future study.

3. Ceramics as model object for cold fusion

Phase transitions

The role of phase transition is active discussed with "classical" scheme pertaining to PdD. But for cold fusion with protonic conductors the influence of this factor is taking new twists.

An important unexpected result of our research of electrical dc and ac conduction consist in the realisation of conditions for rupture change of conductivity charasteristics in doped $ACedO_3$ - ceramics under deuterium atmosphere. This testifies that unknown processes in lattice can occur contributed finally to phenomena observed. Our investigations of current dependences and calorimetric study enable the phase transition in doped ceramic to be found at 445°C [4]. Recently the availability of structural phase transition induced by the temperature variation was confirmed in undoped $BaCeO_3$ by other authors [13, 14]. Thus, the lattice ordering, fluctuations of some characteristics and even non-reproducibility of normal electric properties can be observed. In the latest experiments we obtained some indications on the availability of behavior, which is a close match to phase transition, at other points in the range from 200°C to 1000°C. Of special note is the very large correlation between pass through such temperature points and manifestation of anomalous phenomena.

As mentioned above, during cooling the sample, saturated with deuterium at electrolysis with voltage U = 10 V, we observed a endothermic effect, whereas during a heating the same sample the exothermic pulse process has been detected by the scan microcalorimeter. In line to our method [4], in all experiments the such order of the principle steps was used for heat generation as thermal cycling by means of the inner and outer heaters. This proves conclusively the advantage of the availability of phase transitions in the ceramics. As regards to possible "feedback" for nuclear reactions, the problem of this sort exists. To be sure, the "perfect" structure of the crystal lattice (of the conduction channels) is of vital importance in processes of energy transfer. One possibility of "positive feedback" for the heat generation in PdD systems is described by M.Fleishmann in [16].

Proton traps

A model of multibody fusion for deuteron clustering exists for Pd-deuterium system which looks supportive to some experiments [17]. The problems of particle traps in PdD also have aroused considerable interest. It is interesting to note in this connection that currently striking evidence for the association of protons in doped $SrCeO_3$ was observed using site-selective spectroscopy technique [18]. The quasielastic neutron scattering study of $SrCe_{(0,95)}Yb_{(0,05)}H_{(0,02)}O_{(2,985)}$ was shown, that a sequence of free diffusion and trapping-escape events of protons takes place [19]. The traps with radius of 2,6 Å can immobilize the protons. The nature of proton transport in solids is seen to be not fully understand. Thus their investigation brings us closer to elucidation of cold fusion effect.

Crack formation

The intensive crack formation on the ceramic samples has been observed in all our experiments shown excess heat [2, 4]. This can be du to the compression, to the structure changes or to the existence of shock wave into the sample.

4. Neutron "anti-effect"

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We would like to call attention to one paradox event. Our investigations of neutron emission have shown the influence of background on yield of neutrons from ceramic.

Furthemore, during electrolysis in deuterium atmosphere depending from conditions and chemical purity of ceramic we have observed new neutron "anti-effect". Both before and after experiment we have measured the background during two days. It has adhered to normal distribution. But at thermocycling the abrupte changes in neutron counts rate were fixed into the shielding box with the cell (typical situation is presented on the fig.1). This decay appears near the points of phase transitions and lasts a few tens of seconds, followed by neutron burst. Analogous effect has been observed in the experiments with molten salt according our method, which is described in [20]. The nature of this phenomenon to be investigated.

We have discussed here some examples of use of ceramics as model object to name only a few.

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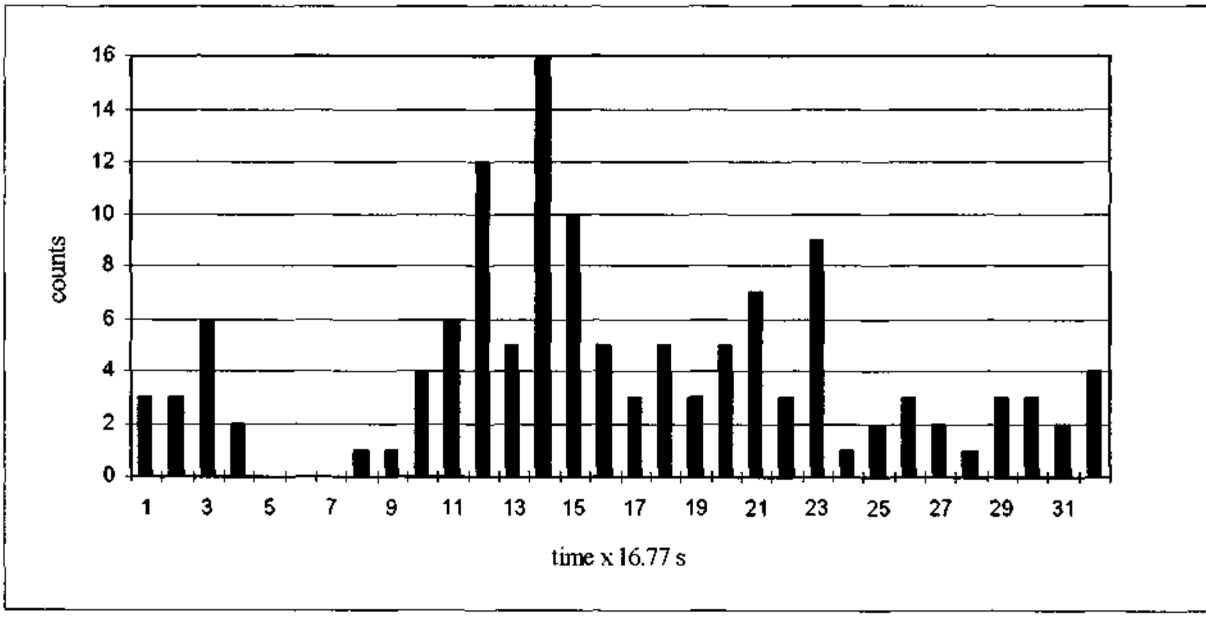

Fig. 1
Yield of neutrons as function of time for one of the experiments.