

**Cold Fusion and anomalous
effects in deuteron conductors during
non-stationary high-temperature electrolysis**

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Abstract

The studies were conducted with the perovskite-type solid electrolytes based on the strontium and barium cerates under hydrogen and deuterium atmosphere. Anomalous effects were found manifesting themselves in the overbackground neutron bursts, excess heat release, phase composition and crystal lattice parameter changes. At 200-750° C the regions of the temperature were identified which accompanied by significant heat evolution that was greater in the deuteron conductors than in the proton conductors.

1. Introduction

It is known /1,2/ that the hydrogen and deuterium absorption and transfer induced electrochemically in the solid oxide electrolytes is attended with the "excess" heat evolution. In specific cases excess heat power has been ranged up to several tens of percent. Meanwhile the poor reproducibility of these experiments was observed. As a result there is no escape from the correct conclusion concerning the causes of anomalous heat liberation. The calculation of the power balance has been pointed to the possibility of the processes associated with overstoichiometrical hydrogen and deuterium concentration in the crystal lattice resulting in the cold fusion or other anomalous phenomena.

In order to obtain the valid data about the reasons of the phenomena observed we carried out the complex investigation of solid electrolytes involving the careful measurements of heat and radiation, the correct determination of above temperature regions, the thorough research of the structure and phase transformations.

In this paper the results of calorimetric and radiometric experiments with samples of Sr(Ba)CeO₃-type proton (deuterium) conductors doped by Dy- and Nd-oxides during high temperature non-stationary electrolysis under D₂ or H₂ atmosphere is presented.

2. Methods

Samples was produced as a tablet 10 mm of diameter and 1-2 mm in thickness with Pd- or Pt-electrodes applied. The design of electrochemical cell used is showed in Fig. 1. As calorimeter the metall cylinder was used. Two hole was bored through its walls for fixing the termocouples. The inner plane heater was placed under sample studied for calibrating calorimeter and providing the temperature gradient through the tablet. The fixed temperature was supported with the outer calorimeter heater. The electrochemical cell was connected with the gas system. It was housed in two-ring neutron detector /3/. Multiple measurements of the neutron background during 1-2 day period showed that the maximum background counts did not exceed 8 pulses for the inner detector ring and 9 pulses for outer detector ring per 16,77 s.

Before the measurements the cell was evacuated with the vacuum pump, then it was heated up to initial working temperature the heat losses being compensated. After this operation the gas was admitted into cell. The heating regime provided a means for the establishment of initial constant temperature. Then the calorimeter calibration was carried out at the several fixed power loads (50, 100, 150 and 200 mW) on the inner heater. The calibrating curve is approximated by equation $W=f(dT)$ where W and dT are the heat power of the inner heater and the after temperature of the calorimeter. In all cases the same order of the principle steps in the experimental procedure was used.

I. After achievement of constant temperature over the cell the invariable electrical potential was applied to the electrodes for producing the electrolytic process. Within a few hours heat quasiequilibrium have been established.

II. Then the electrolysis was continued with the periodic sign-variable /reversible/ electrical potential supplied.

III. When fixed thermal steady-state condition the sample was sharply heated up to the cycling temperature T_{cycl} , the reverse electrolysis being contined.

IV. Further thermal cycling was conducted by means of the inner and outer heaters in the range of temperature from 200 ° C to T_{cycl} . For the same sample all above experimental stages has been repeated a few times. Throughout the whole experiment the calorimeter temperature and that of sample surface was being steadily recorded as well as the time distribution of the neutron counte rate with digitization time of detection of 4 microseconds. By means of crate CAMAC all the data is stored in PC memory for subsequent processing. The heat power was determined with the calibrating curves found for both stationary conditions and non-steady-state ones. The typical examples of $dT-t$ and $W-dT$ dependences are presentad in Fig.2 and 3.

A wariety of ceramic samples with the Pt- and Pd- electrodes was examined under different gas atmosphere. It was recently shown / 4/ that the perovskite-type

oxide electrolytes with about the same chemical composition as the ones studied by us has been transformed to the proton conductors under the influence of H₂-gas or H₂O-vapour medium. Therefore in the subsequent discussion we shall use the terms "protonconducting" and "deuteronconducting" ceramic samples with respect to the ones researched under H₂ or D₂ gas atmosphere.

Besides the additional investigations of heat releasing processes during the electrolysis under hydrogen and deuterium atmosphere were carried out using the scanning Calvet-microcalorimeter with the constant heating rate in the temperature range from 200 to 750°C.

3. Results and Discussion

Deuteronconducting electrolyte (No.1).

Many-day experiment was being conducted in above consequence. Under heating and cooling doped SrCeO₃-sample the unknown phase transition was found at the 445°C. All forthcoming operations involving current reversing and heat cycling was conducted with special attention to the temperature changes and neutron flashes close to the phase transition point. The runs were broken when the current density at constant electrical potential sharply diminished. This fact was evidence of scaling electrodes off the oxide tablet.

Anomalous heat effects and overbackground neutron bursts were found in this experiment. They were observed with supplied constant electrical potential about 10V. The heat power released exceeded one expended for producing electrolytic process by 10-1000% depending on way of electrical current loading. Within 18 hours the six events emitting neutrons as the individual bursts out the experimental errors were observed.

Deuteronconducting electrolyte (No.2).

In this run with unlike sample of deuteronconducting ceramics we were deciding the problem to obtain additional information on the heat evolution under non-steady-state heating or cooling regime as well as to fix temperature in situ. Only distinction from the run No.1 was the dynamical dT-t curves was recording for every heat power given up to the stationary temperature. Besides, inner surface of two-ring neutron detector was controlled thermostatically.

The results of these examinations were used to calculate excess heat liberated during electrolysis. To do this the value of heat power released (W_{libr}) compared with one expended (W_{exp}). When electrolyzing without thermocycling

$$W_{\text{exp}} = W_{\text{outer heater}} + W_{\text{electr}} \text{ while when electrolyzing with thermocycling}$$

$$W_{\text{exp}} = W_{\text{outer heater}} + W_{\text{electr}} + W_{\text{inner heater}} \text{ Then the relative excess heat effect is}$$

$$\frac{W_{\text{libr}} - W_{\text{exp}}}{W_{\text{electr}}} \times 100\%$$

In our calculations the initial stationary temperature was taken as the reference one. The heat power of outer heater was constant throughout every experiment. It was expended for the compensating thermal losses. The heat power put in reverse electrolysis was evaluated by maximum electrical current observed. Its real magnitude could be not correctly found without using special integrating recorder. This naturally decreased the real excess heat effect. The results obtained is listed in Tabl. 1-4.

Table 1. The electrolysis with time-constant electrical potential.

$t,$ <i>min</i>	$W_{\text{outer heater}}$ W	W_{electr} (max), W	W_{exp} , W	W_{libr} , W	$\frac{W_{\text{libr}} - W_{\text{exp}}}{W_{\text{electr}}}$, %
5	14.686	0.1276	14.813	14.838	20
10	14.686	0.1150	14.801	14.823	19
20	14.686	0.1042	14.790	14.806	15
30	14.686	1.0360	14.789	14.799	10
360	14.686	0.0790	14.765	14.788	29

Table 2. The electrolysis with reverse electrical load ($U=10$ V)

$t,$ <i>min</i>	$W_{\text{outer heater}}$ W	W_{electr} (max), W	W_{exp} , W	W_{libr} , W	$\frac{W_{\text{libr}} - W_{\text{exp}}}{W_{\text{electr}}}$, %
60	14.686	0.016	14.702	14.734	200
360	14.686	0.015	14.071	14.732	206
24 hours	14.686	0.014	14.700	14.763	450

Table 3. The electrolysis with reverse electrical load ($U=41$ V)

$t,$ <i>min</i>	$W_{\text{outer heater}}$ W	W_{electr} (max), W	W_{exp} , W	W_{libr} , W	$\frac{W_{\text{libr}} - W_{\text{exp}}}{W_{\text{electr}}}$, %
30	14.686	0.238	14.924	15.103	75
75	14.686	0.238	14.924	15.026	43

Table 4. The electrolysis with reversing electrical load and thermocycling

t, min	$W_{\text{outer heater}}$, W	$W_{\text{inner heater}}$, W	$W_{\text{electr (max)}}$, W	W_{exp} , W	W_{libr} , W	$\frac{W_{\text{libr}} - W_{\text{exp}}}{W_{\text{electr}}}$, %
N1 5	14.686	23.994	2.11	40.800	43.300	118
N1 10	14.686	23.994	1.057	39.737	40.400	62.7
N2 5	14.686	24.108	1.283	40.071	41.100	80.2
N2 10	14.686	24.222	0.585	39.490	39.600	18.8

Total errors in finding heat power are $\pm 10,5\text{mW}$ for electrolyzing regime without thermocycling and $\pm 154 \text{ mW}$ for one with thermocycling. The overbackground neutron bursts of duration of 100 microseconds were observed in ten hours from beginning the electro lysis. The eight exceeding events (Count number is greater than 10) were registated within time interval 16.7 s during 32 hours. A half of them was found for direct electrolysis, while the others were measured for reverse electrolysis.

Protonconducting electrolyte

According to the above procedure the experiments were carried out with the same ceramic probe under H_2 -atmosphere. The thermal treatment and evacuation were brought about to remove residual D_2 -gas from the sample.

After control calibrating calorimetr and establishing heat steady-state condition the experiment was continued. The calculation showed the heat power released was lower than one for deuteronconducting sample. The excess heat effect was not found in the case of the electrolysis with direct electrical supply while one was fixed under reverse electrolyzing and thermocycling. The last fell down for a short time the natural neutron background was not exceeded.

Microcalorimetric investigation

The studies showed three temperature regions with the anomalous thermal effects for the both deuteron and proton conductors in the temperature range from 200 to 750 ° C (See fig.4). The heat evolution for deuteron conductor is greater than proton one. One can suppose the phase transition (I) are occured. The cathastrophic change of the heat liberation can be associated to some processes at phase transitions in the systems of ceramics - isotopic hydrogen. To elucidate these phenomena the additional investigations ough to conduct.

The X-ray diffraction studies.

The X-ray examination with deuteron conducting solid electrolytes fixed change of the phase composition and crystal lattice parameters after electrolysis. In particular, for the samples with the significant excess heat release two separate phase was found including SrCeO_3 -type phase and CeO_2 -type one. As a rule for the samples under thermocycling the crack formation was clearly observed.

References

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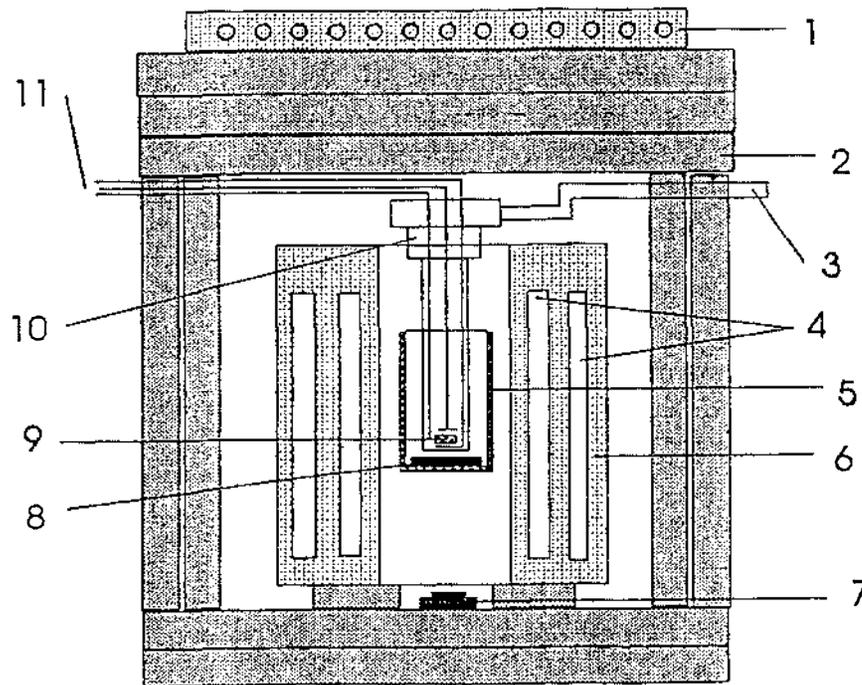


fig. 1.

- 1 - Block of detectors Si-19N.
- 2 - Neutron protective wall (3% boron).
- 3 - Vacuum-pumping system tube.
- 4 - Two rings of detectors SNMO-5.
- 5 - Heat shield.
- 6 - Moderator.
- 7 - Ventilator.
- 8 - The heater.
- 9 - The sample.
- 10 - The working cell.
- 11 - Two current conductors and thermocouple.

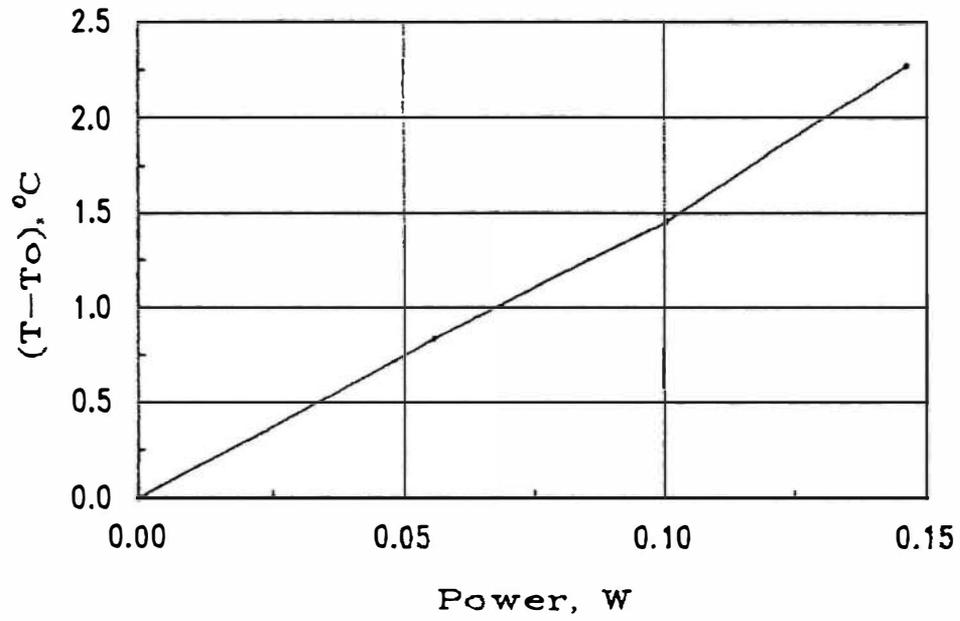


Fig.3

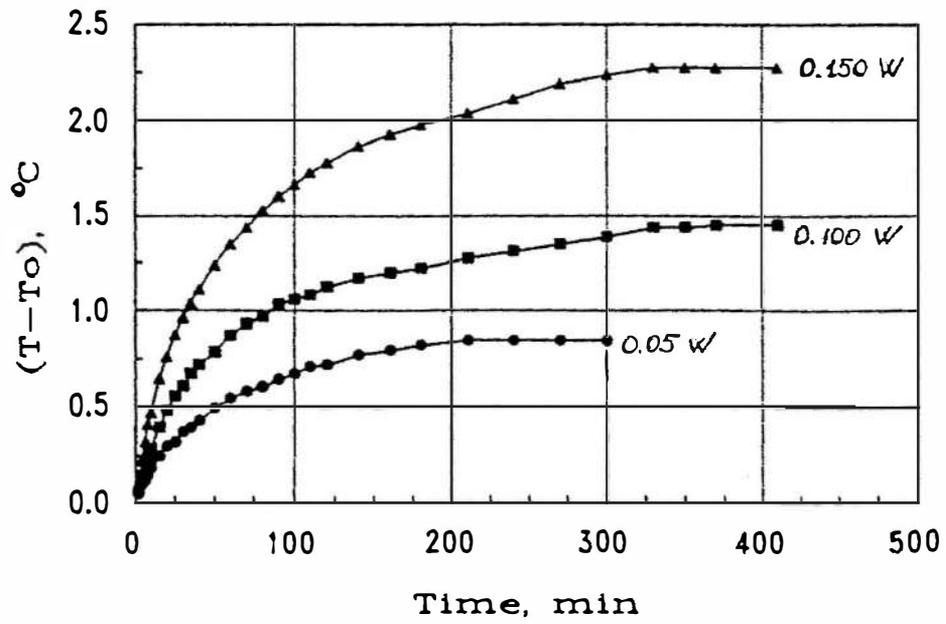


Fig.2

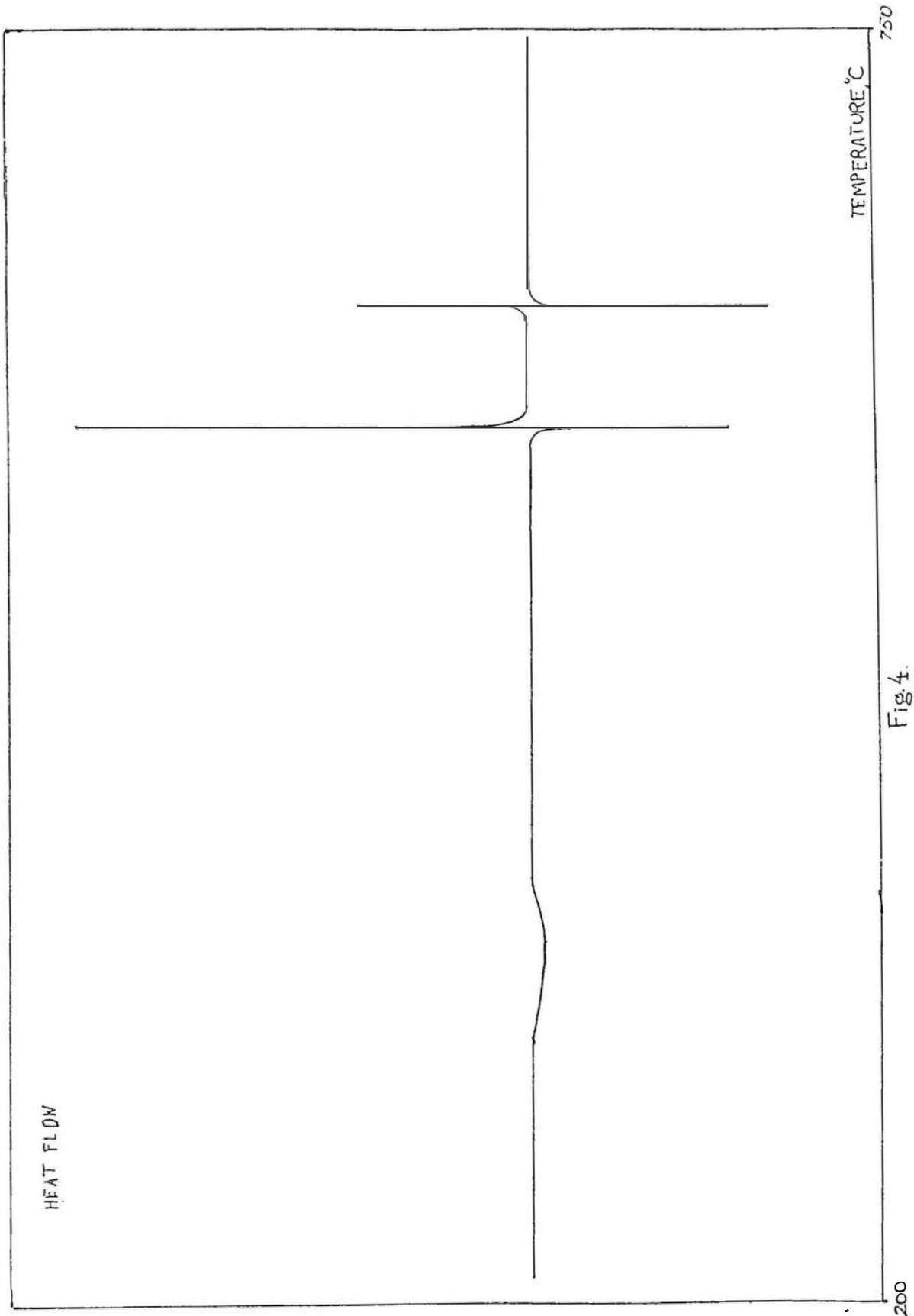


Fig. 4.