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A CONFIRMATION OF ANOMALOUS THERMAL POWER GENERATION FROM A PROTON CONDUCTING OXIDE

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Abstract

The claims of Mizuno and collaborators, and the earlier claims of Biberian and Forrat, that excess thermal power can be developed by proton-conducting oxides held in deuterium gas at elevated temperatures are important because thermal power generated at high temperatures can be converted to other forms of power with greater Carnot efficiency than thermal power at lower temperatures. Therefore, a Seebeck calorimeter operating at 400°C was constructed to attempt to verify these claims. This calorimeter, whose operation is independent of the spatial distribution of power sources and of the thermal conductivity of the gas, is described.

The calorimeter was used with specimens of nominal composition $SrCe_{0.9}Y_{0.08}Nb_{0.02}O_{2.97}$ supplied by Dr. T. Mizuno. Two of these specimens produced positive deviations from the calibration curve by more than four standard deviations so that thermal power was produced that was greater than the d.c. power of alternating polarity supplied to the specimen. In several episodes excess power was produced without supplying any d.c. power.

Verification of the claims has been achieved. It remains to increase the reproducibility and the power output of the technique, as well as to achieve understanding of the underlying mechanism of the phenomenon.

Introduction

Beginning with the initial work of Pons and Fleischmann (1), a number of reliable calorimetric determinations have been carried out (2,3) that have demonstrated that in a variety of processes it is possible to obtain more thermal power than can be accounted for by the electrical power put into the system. At the Fourth International Conference on Cold Fusion, T. Mizuno (4) announced the generation of excess thermal power from a perovskite oxide held in deuterium gas at temperatures about 400°C (see also (5)). In these experiments the oxide specimen bathed by D_2 gas is maintained at the desired temperature by measured, constant electrical power delivered to a small furnace inside of a gas-tight enclosure. Then a voltage whose polarity is alternated at a frequency between 10^{-4} and 1 Hz is applied across the specimen thickness, generating a small, measured electrical power in the specimen. In some, but not all such experiments (about 12 out of 80 attempts), the specimen temperature was observed to rise considerably above the value consistent with the electrical power furnished to the specimen.

Because thermal power generated at high temperatures can be converted to other forms of power with greater Carnot efficiency than thermal power at lower temperatures, Mizuno's generation of excess power is particularly interesting. In addition, Biberian (6) following earlier work by Forrat (7) has also claimed to have generated excess power with $LaAlO_3$ in D_2 gas by a similar process. For these reasons it has seemed important to attempt to verify claims of the production of excess power from perovskite oxides. The present work has been done with a newly constructed Seebeck calorimeter using specimens of nominal composition $SrCe_{0.9}Y_{0.08}Nb_{0.02}O_{2.97}$ made and supplied by Dr. T. Mizuno of Hokkaido University.

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The Seebeck Calorimeter

The principle of Seebeck calorimetry is the generation of a thermoelectric emf by a large number of thermocouple junctions connected in series in response to a temperature difference, ΔT, across the walls of an enclosure that totally surrounds a source of thermal power. The multiple thermocouples are arranged such that junctions of one polarity lie on the outside surface (that contacting a heat sink) of the enclosure, and junctions of the opposite polarity lie on the inside surface of the enclosure. If the thermocouple junctions completely and densely surround the source of thermal power and the thermal conductivity of the material of the enclosure is K, the thermal power transmitted to the constant temperature heat sink is $P_{out} = K\Delta T$, where ΔT is the average temperature difference across the enclosure walls as integrated by the multiple thermocouples, and at steady state P_{out} = thermal power generated within the enclosure. In practice it is, of course, impossible to cover the entire wall area of the enclosure since power leads, gas ducts, etc., must have access to the interior of the enclosure. Hence, in general at steady state $P_{source} = P_{out} = K\Delta T + a(T_i - T_s) + b(T_i - T_L)$, where T_i, T_s, and T_L are the temperatures of the source, the heat sink, and the laboratory, respectively. With proper design, the second and third terms can be rendered small, and the relation between P_{source} and the Seebeck signal, E_s, (which is linear in ΔT) can be established by calibration by using a known heat source.

The apparatus consists of three principal units. These are a gas-tight envelope for the specimen and furnace, the Seebeck thermoelectric device, and the thermostatted environment. These are discussed separately. The envelope (the reactor) for the specimen is a stainless steel closed cylinder welded to a stainless steel flange which mates via a copper gasket with another stainless steel flange through which enter the power leads for the small furnace that surrounds the specimen, and for the specimen and for an auxiliary heater, as well as a chromel-alumel thermocouple and a stainless steel tube which leads via swagelock fittings to a vacuum and gas-handling system made entirely of metal. The perovskite disc specimen, sandwiched between either thin palladium or platinum discs, is supported by perforated copper plates within the furnace made of nichrome wire wound on a spirally grooved ceramic tube. The specimens supplied by Dr. T. Mizuno measure about two cm in diameter by about 1 mm in thickness. The faces of the disc have been thinly coated with metal, either Pd or Pt Mo. Within the furnace is also a small coin-shaped ceramic cast about a spirally wound nichrome wire made and supplied by Mr. Jeff Driscoll. This device serves as an auxiliary heater used for calibration of the calorimeter. The junction of the chromel-alumel thermocouple is in the gas phase between the specimen and the inside of the furnace tube.

The Seebeck calorimeter itself is a parallelopiped enclosure made of machineable ceramic, and it surrounds the reactor on five sides. The sixth side, its base, rests on insulating ceramic. Through 1/16 inch diameter holes in each of the five sides a continuous wire of alternating chromel and alumel segments is threaded in such a way that the inside surface of the ceramic parallelopiped has 355 thermoelectric junctions and the outside surface has an equal number of junctions of opposite polarity. The thermoelectric emf developed by the temperature difference between the inside and the outside surfaces, integrated over the five sides, is measured both by a digital millivoltmeter and by a sensitive strip chart recorder. The latter continually records the difference between the thermoelectric emf and an applied adjustable constant voltage in order to increase the sensitivity of the recorder to small variations of the thermoelectric emf. The purpose of the strip chart recorder is to have a record of the time dependence of the thermoelectric signal, E_s. About 5 hours are required to attain steady state. Because of the greater sensitivity of the digital voltmeter, its readings of E_s at steady state are taken for plots of E_s vs. input power and subsequent analysis.

At steady state, that is when temperatures everywhere in the system are time independent, the thermoelectric emf is a measure of the power generated within the reactor. Clearly this necessitates a time-independent temperature of the environment that serves as a heat sink. This is accomplished by an insulated cylinder that envelopes the Seebeck calorimeter. It is fitted with a large-area heater and an air fan driven by a constant-speed motor. The average temperature of the air within this insulated jacket is maintained constant by a controller, operating between two adjustable power levels, which uses the output of four thermocouples connected in series as the distributed sensing element. In order to make the Seebeck calorimeter less sensitive to fluctuations in air movement between regions of different temperatures, the Seebeck box is closely surrounded by a five-sided enclosure made of copper sheet which causes the Seebeck system to "see" the average temperature of the circulating air.

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All wire connections and the tube for evacuation of the retort and admission of gases to it are led out below the retort through an opening in the insulated platform that supports all of the systems described above. The platform in turn is supported by a stand which is entirely surrounded by an insulating skirt. A constant-current d.c. power supply furnishes power to the furnace within the retort. Separate d.c. power supplies furnish power to the auxiliary heater and to the specimen. In all cases the power delivered is measured by digital ammeters and voltmeters, taking care that the same instruments and settings are used both in calibrations and in the experimental runs. The signal from the thermocouple within the reactor is read by a digital millivoltmeter. The temperature of the circulating air is continuously recorded and also occasionally measured by a hand-held Fluke voltmeter.

Calibration of the calorimeter is accomplished by furnishing measured electrical power to the furnace and to the auxiliary heater and measuring E_S at steady state. By varying the ratio between the power supplied to the furnace and that supplied to the auxiliary heater it was verified that E_S is independent of the spatial distribution of the power sources, whereas the reading of the internal chromel-alumel thermocouple depends upon that distribution. The calibration is found to yield a linear E_S (P) relation, where P is the total input power. Furthermore, the E_S (P) relation does not depend on the thermal conductivity of the gas within the reactor , whereas the reading of the internal thermocouple is a strong function of the nature of the gas phase, and also of the spatial distribution of the sources of power. The regression lines fitted to the calibration data are characterized by very small standard deviations of the order of 0.1 mV for signals of the order of 70 mV.

Results and Discussion

The initial experiments with the Seebeck calorimeter were done by first establishing the E_S (P) relation with D_2 gas without the perovskite specimen in place. The reason for this precaution is that in earlier work with an isoperibolic calorimeter some results seemed to show generation of excess power before d.c. power was supplied to the specimen. After calibration without the specimen, the specimen was put in place within the reactor, the apparatus was reassembled and an experimental run was carried out. Generation of excess power is judged by comparing the E_S produced by a given value of P with the E_S value given by the calibration line for that value of P. The experimental run with a specimen in the reactor consisted of heating the reactor by means of the furnace while continually evacuating the reactor by means of a mechanical pump. After reaching a temperature in excess of 400°C deuterium gas was admitted to a pressure between 0.1 and 0.3 atm and a steady state was allowed to be attained. Direct current of alternating polarity was then applied to the specimen and steady state was again awaited. The frequency of alternation of polarity was between 0.1 and 0.003 Hz. The temperature of the air surrounding the Seebeck box was maintained constant at 106°C.

Many experiments were done in this fashion while the performance of the calorimeter was continually improved. Although some indications of the generation of excess power were obtained during this period none can be considered reliable. Final modifications of the calorimeter produced reliable operation. At this stage an experiment was carried out which yielded excess power (Experiment X). First a calibration was carried out, without the specimen in place, with deuterium gas in the reactor. Then the apparatus was totally disassembled, re-assembled and another calibration, again without a specimen in the reactor, was made. The two calibrations for E_S(P) agree with each other and can be fitted by a straight line characterized by $r = 0.9988$ and standard deviation $\sigma = 0.116$ mV. A perovskite specimen was then mounted within the reactor and an experimental run at about 410°C was carried out which is detailed in Table 1. The first point established without d.c. current into the specimen falls within one standard deviation from the calibration line, giving confidence that the calibration is valid for the experiment with the specimen in place. After this, 0.009 W of d.c. power with its polarity alternating at about 0.008 Hz was supplied to the specimen; the power to the furnace was adjusted attempting, unsuccessfully, to keep the total input power constant. This produced an E_S value above the calibration line, and the positive deviation persisted after the d.c. power to the specimen was turned off. After this, the experiment was continued at times with, and at other times without, d.c. power to the specimen. The steady-state points are all considerably above the calibration line. One can have considerable confidence that the six data points in Table 1 that lie at more than four sigma values above the calibration line exhibit the generation of

excess power. For orientation, a deviation, δ, of +0.6 mV represents excess power equal to 0.65 W which is considerably larger than the d.c. power into the specimen ranging from 0.047 to zero watt. Table 4 displays the values of excess power calculated from the positive deviations from the calibration line. The episodes characterized by more than 4σ deviation from the calibration line produced excess power over a cumulative time of 90 hours.

During the period leading to the successful experiment described above it was noted that now and then an $E_S(P)$ calibration was obtained after a disassembly/re-assembly sequence that was somewhat different from what had been obtained prior to that operation despite great care to reproduce exactly all features of the assembly. To avoid this possible source of uncertainty, it was decided to calibrate with a specimen already within the reactor, but using helium within the reactor to avoid the possible generation of excess power during calibration. Then without disturbing the apparatus the helium was evacuated and replaced by deuterium for the search for excess power generation.*

Six experiments were carried out as described, each one with a calibration using helium for which the standard deviation, σ, was calculated. The distribution of the deviations of the individual calibration points, characterized by the number, n, of sigmas, is shown in Table 2 in which the calibration data of experiment X are also included for completeness. The distribution of the n-values of all the calibration points is roughly Gaussian. Table 2 also displays the distribution of n-values for the individual data points of the power runs with deuterium of the six determinations that had been preceded by calibrations with helium, as well as for the data of Table 1. It is noted that all but one entry represent positive deviations, and that the distribution is heavily weighted toward large values of n. Most of the large values arise in two experimental runs, the one labeled X and detailed in Table 1, and run B, detailed in Table 3, from the sequence of six experiments that employed helium for the calibrations. Table 4 displays the values of excess power calculated from the positive deviations given in Table 3. Again, we pay attention only to the data characterized by more than 4σ deviation from the calibration line and note that excess power can be developed even without alternating d.c. power into the specimen. It is worthwhile to remark that the same perovskite specimen was used in experiment X (Table 1) first, then later in experiment B. This specimen was coated by Dr. Mizuno with 300 nm of platinum by sputtering. It is also worth recording that run B developed excess power only after some days during which the determinations were on the calibration line, after which a lengthy, high-temperature continuous evacuation of the reactor and heating of the vacuum lines were carried out. After obtaining the data given in Table 3 for Run B, the calorimeter was calibrated again with the specimen undisturbed in place and under helium, yielding points on the same calibration line as before.

These data provide strong evidence that under some conditions this strontium-cerium based oxide in an atmosphere of deuterium gas can produce thermal power, as claimed by Mizuno and collaborators. However, it is clear that the ratio of experiments with which success in generating excess power can be claimed to those which yield only points lying on the calibration line is small. Mizuno et al. have reported a similar experience. The factors that lead to this lack of reproducibility are unknown, but it is suspected that they are related to details of specimen preparation. In the present experiments much variation among the specimens was noted in the electrical resistance across the thickness of the specimens as well as of the faces of the discs, and also in the appearance of the metallic coatings on the disc faces. It is believed that success in developing reproducibility depends on learning how to produce the required characteristics in the perovskite, whether these be composition, dopant distribution, crystallite size, grain boundary structure and composition, etc. It is emphasized that the calorimetric method employed in this kind of work should not depend upon a measurement of temperature because the thermal conductivity of the ambient gaseous phase depends markedly upon its composition and this can change in the process of experimentation, leading to incorrect conclusions.

The magnitude of the thermal power generated in these experiments is small and clearly not interesting from a technological point of view. However, at the present stage establishment of the phenomenon is important. Much work is needed to increase the reproducibility and the power output, as well as to achieve understanding of the mechanism which is currently completely mysterious.

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TABLE 1
Details of Experiment X

d.c. power W	P, Total Input Power, W	E_S, mV	Duration of episode, h	δ, mV	n
0	65.20	73.60		+0.11	1
0.009	65.14	73.75		+0.32	2.7
0	64.83	73.72	17	+0.57	4.9
0.015	64.765	73.75	7	+0.66	5.7
0	64.77	73.74	16	+0.65	5.6
0.036	64.656	73.63	10	+0.64	5.5
0	63.44	72.12		+0.24	2.1
0	66.88	75.55	23	+0.52	4.5
0	68.22	76.61		+0.36	3.1
0	68.31	76.63		+0.30	2.6
0.039	68.36	76.67		+0.29	2.5
0.047	68.18	76.74	17	+0.52	4.5

Notes: E_S = Seebeck emf

δ = deviation of measured E_S of the poewr run from E_S calculated from regression line, E_S = 13.187 + 0.9152 P, for the calibration specific to this power run, for which r = 0.9988 and σ = 0.116 mV.

$n = \delta/\sigma$

The tabulated numbers are listed in the order of experimental measurement.

TABLE 2
Distributions of n values ($n = \delta/\sigma$)

	For Power Experiments of Runs X and B		
n-values	all calibration points	Experiment X	Six D_2 runs
7.0 to 7.5			2
6.5 to 7.0			
6.0 to 6.5			
5.5 to 6.0		3	
5.0 to 5.5			
4.5 to 5.0		2	1
4.0 to 4.5			1
3.5 to 4.0			1
3.0 to 3.5		1	2
2.5 to 3.0		3	
2.0 to 2.5		1	4
1.5 to 2.0	1		2
1.0 to 1.5	5	1	4
0.5 to 1.0	5		4
0 to 0.5	10		5
-0.5 to 0	6		
-1.0 to -0.5	6		1
-1.5 to -1.0	2		
-2.0 to -1.5	4		

Notes: The second column refers to the data points of eight calibration runs. The third column refers to the data points (episodes) of power run X which followed two calibration runs using D_2 gas without the specimen in place. The fourth column refers to data points (episodes) of the six power runs each of which was preceded by a calibration run using He gas with the specimen in place.

TABLE 3
Details of Experiment B

d.c. power, W	P, total power, W	E_S, mV	Duration of episode, h	δ, mV	n
0	72.11	77.31		+0.073	1.3
0.25	72.49	77.61		+0.086	1.5
0.25	72.60	77.61		+0.003	0.05
0	79.423	82.87		+0.125	2.2
0.399	79.896	83.33	16	+0.229	4.1
0.432	79.876	83.49	24	+0.404	7.3
0.484	79.903	83.50	25	+0.393	7.1
0	79.40	82.98	16	+0.252	4.5
0	79.40	82.78		+0.052	0.9

Notes: E_S = Seebeck emf
δ = deviation of measured E_S from E_S calculated from regression line, $E_S = 22.93 + 0.75312$ P, for the calibration specific to this experiment, for which $r = 0.99982$ and $\sigma = 0.0556$ mV.
$n = \delta/\sigma$, where $\sigma = 0.0556$ mV.
The tabulated numbers are listed in the order of experimental measurement.

TABLE 4
Excess Power Energy Calculated for the Episodes Exhibiting Large Positive Deviations From the Calibration Line

Input d.c. Power, W	n, the Number of Standard Deviations Above the Calibration Line	Excess Power, W	Duration of Episode, h	Integrated Excess Energy, kJ
Experiment X				
0	4.9	0.62	17	37.9
0.015	5.7	0.72	7	18.1
0	5.6	0.71	16	40.9
0.036	5.5	0.70	10	25.2
0	4.5	0.57	23	47.2
0.047	4.5	0.57	17	34.9
Experiment B				
0.399	4.1	0.30	16	17.3
4.32	7.3	0.54	24	46.7
0.484	7.1	0.52	25	46.8
0	4.5	0.33	16	19.0