Study of Operating Characteristics of Pyrotechnic Reserve Power Source Based on Magnesium and Zinc

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Abstract

This paper presents the results of studies of operating parameters of pyrotechnic reserve power source (PRPS). This battery was activated by the pyrotechnic compositions contained in the electrodes. Once the ignition impulse worked, the pyrotechnic compositions took fire immediately and melted the electrolyte. Then the rest pyrotechnic compositions served as anode and cathode. The battery began to discharge. The following characteristics of PRPS were evaluated during the study: release time to operating regime of the electric current, the duration of the PRPS work and initiation temperature of PRPS. A detailed evaluation of the $Mg/LiF/PbF_2$ electrochemical system and $Zn/LiF/PbF_2$ one is undertaken. Test results show that the electric current value using powder of zinc and granular zinc in these experiments was 0.179 A and 0.1 A, respectively, and the operating time at these values of elecrtic current was 40 and 151 sec, respectively.

1. Introduction

Chemical sources are divided into primary, secondary and reserve, as well as electrochemical generators. Primary power sources (galvanic cells and batteries), generally, enable single use of energy of chemical reagents. Some modifications of electrochemical cells and batteries allow short-term reuse of chemical reagents after the electric energy charge. PRPS (electrochemical generators) based on pyrotechnic content are a variety of chemical power sources. Typically, PRPS includes direct conversion of chemical energy of electrode with pyrotechnic composition into electrical energy. The anode and cathode pyrotechnic compositions consist of fuel, oxidant, and an electrolyte. Anode includes pyrotechnic charge with an excess of fuel, and the cathode – with an excess of oxidant. Anode and cathode cells of PRPS are divided by separator and possess metal contact plates to connect to the external electric circuit [1]. Such source is capable to be in standby (passive) regime and generate electrical energy only after initiation.

PRPS is able to continuously generate electric current in the form of short and long charge [2]. In contradistinction to galvanic cells and batteries, electrolyte in PRPS never keeps in bound with electrodes. Currently, PRPS are used in various fields of technology: spacecraft power supply, in facilities operating in areas with a low temperature, hybrid automatic devices, etc. [3]. This is due to a number of advantages and opportunities, such as autonomy, small size and the relative ease of manufacture [4]. As the electrolyte material can be used capillary porous membrane containing liquid electrolyte, dry mixture of electrolyte salts or crystalline hydrates [5].

PRPS enable single use of energy of chemical reagents. As mentioned above electrolyte in PRPS never keeps in bound with electrodes. It keeps in liquid state (in glass, plastic and metal ampoules) or in solid state in the inter-electrode gaps [6]. During preparation for the work, these ampoules are destroyed by compressed air or combustion. In addition, an electric or pyrotechnic heating melts crystals of solid electrolyte. Storage life of modern PRPS is more than 10–15 years [7].

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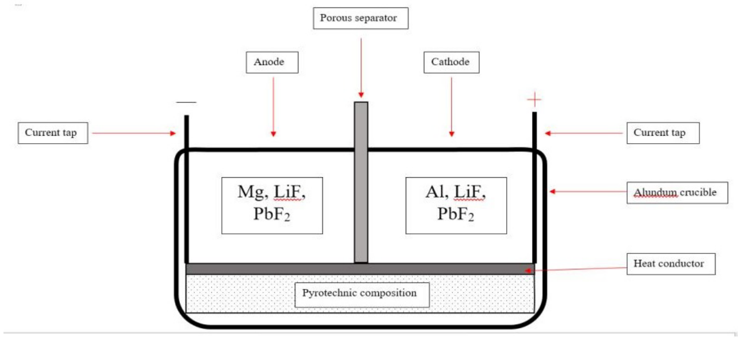

Fig. 1. Scheme of PRPS [8].

Electrochemical generators or fuel cells are a type of chemical current sources. Electrochemical generators are capable for a long time continuously generate electricity by converting energy of chemical reagents (gaseous or liquid), that enter into generator from outside [7]. Figure 1 shows the principal scheme of PRPS.

The aim of this work is to develop PRPS, as well as the study of the influence of the thickness of the asbestos separator on the operating characteristics of the studied system.

Currently, the potential opportunities of PRPS are realized far from being full. There are targets for output voltage and current increase, time-to-work regime reduce, increase of operating time in optimal regime and others.

2. Experimental

In this paper, investigated PRPS provides galvanic cells as a pyrotechnic charge in the cathode and anode. Provided research can be divided into several stages:

1. Influence investigation of the separator thickness on the operating parameters of the PRPS based on magnesium;
2. Study of the PRPS characteristics based on zinc, such as operating time at optimal regime, release time to the operating mode.

In the work fluorine-containing reagents were used – LiF, PbF_2 ("Vekton" company, Saint Petersburg, 99% purity). As a pyrotechnic substances used aluminum (PA-4 mark powder, 99% purity, 65-micron size) and metallic magnesium (99% purity).

Electrochemical reaction, which occurs in one cell, is as follows:

$$Mg - 2e \rightarrow Mg^{2+} \quad (1)$$

Electrochemical cell cathode reaction:

$$Pb^{2+} + 2e \rightarrow Pb \quad (2)$$

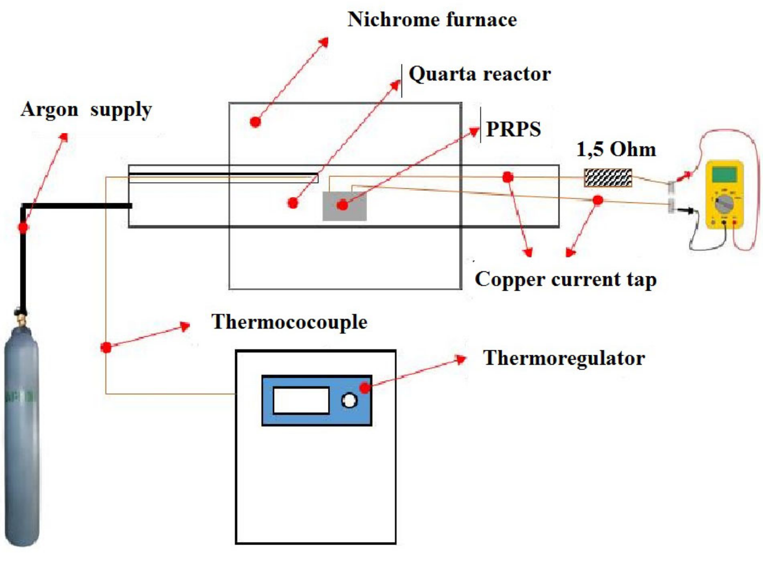

Fig. 2. Principal scheme of experimental setup.

The overall electrochemical reaction in the cathode-anode cell:

$$PbF_2 + Mg \rightarrow MgF_2 + Pb \quad (3)$$

Figure 2 represents setup scheme. For initiation nichrome furnace was used. Initiation temperature was around 650 °C. Cathode-anode cell was placed into the quartz reactor with diameter of 60 mm and 1000 mm length. Experiments were carried out under an inert atmosphere of argon.

Copper current taps were connected to multimeter. Alundum crucible with 25 mm diameter and 30 mm height was used as a case for the cathode-anode cell. The separator was made of compressed asbestos 2 and 0.8 mm thick. The anode contains the following components (mass, %): 58.0 PbF_2; 22.0 Mg; 20.0 LiF. Cathode content (mass, %): 89.52 PbF_2; 3.48 Al; 7.0 LiF. Mass for both cathode and anode was 10 gr.

Figure 3 shows external view of nichrome furnace and quartz reactor.

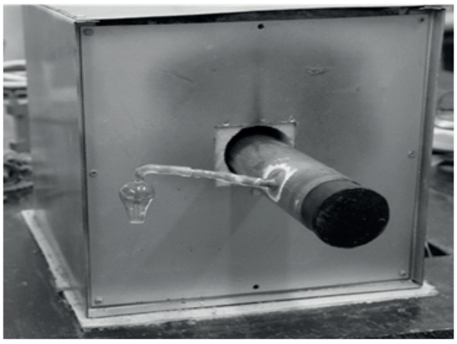

Fig. 3. Nichrome furnace with quartz reactor.

Alundum crucible with initial cathode and anode was placed into the quartz reactor. Copper current taps were connected to multimeter. Figure 4 reveals the photographs of samples before and after experiments.

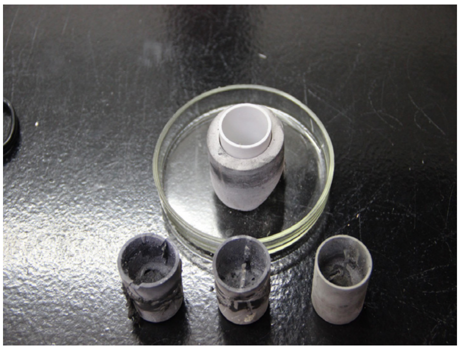

Fig. 4. External view of cathode-anode cells before and after experiments.

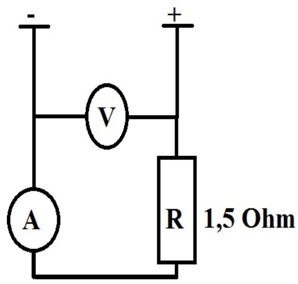

Fig. 5. Scheme of current and voltage measurement in the PRPS system.

It should be noted that a nickel current taps were used as the current collector, which in the following experiments was replaced by graphite rods with copper current taps. This decision was taken due to nickel reacts with fluorine, which in turn leads to increase of resistance.

Figure 5 shows a schematic diagram of an electrical circuit of current collection from PRPS.

To study the effect of separator thickness on the operating parameters of the PRPS the dependences of voltage and current on the time at different thicknesses of asbestos separator were studied.

3. Results and discussion

3.1. Influence of separator thickness on the operating parameters of the PRPS based on magnesium

As a result, dependences of voltage and current on the time at different content of PRPS were obtained. First of all, dependence of separator thickness on the current was obtained since such parameter plays important role in reaction flow.

The first series of experiments were carried out using asbestos separator with 2 mm thick. Experimental data is shown in Table 1.

Table 1
Voltage and electric current values with 2 mm thick separator

№ of experiment	Electric current(A)	Voltage(V)
1	0.03	0.42
2	0.08	0.35
3	0.05	0.48
4	0.03	0.5
5	0.06	0.2

From Table 1 it is seen that electric current values are very low for such type of PRPS. Obviously, this is due to the fact that the increased thickness of the separator prevents the free passage of the charged particles generated during the electrochemical reaction. There were five series of experiments with 2 mm thick separator.

Next step was the study of operating characteristics of the PRPS with 0.8 mm thick separator. Results of experiments are given in Table 2.

Table 2
Voltage and electric current values with 0.8 mm thick separator

№ of experiment	Electric current(A)	Voltage(V)
1	0.35	0.42
2	0.43	0.52
3	0.48	0.73
4	0.5	0.64
5	0.41	0.59

From Table 2, it follows that with a separator of 0.8 mm thick electric current value is much higher in comparison with the values given in Table 1, where the thickness asbestos was 2 mm.

Based on the experiments it can be concluded that by decreasing separator's thickness the electric current could be increased. By reducing thickness of the separator 2 times, there is an increase in the electric current 10 times. In [9] authors carried outstudy of characteristics of the separator at different concentrations of MgO, as a result,reduced activation temperature and the thickness of the separator [10] had effected on the current and voltage values.

In [11] authors made PRPS, that contains battery mounted in the case and having two isolated current taps. The battery of electrochemical cells has the form of pyrotechnic charges with an excess of oxidant in the cathode and excess of fuel in anode, separated by asbestos separator. The separator was dispersed in an electrolyte comprising metal fluorides and zirconium dioxide. Electrochemical cells connected in series through the current taps placed there between metal discs in the form of foil with thickness of 11–13% of the thickness of electrochemical cells and connected with electric igniter by firing circuit comprising pyroheaters ends connected igniting ribbon. The technical result is improvement of functional reliability of PRPS.

However, the objective of this work consists in increasing operating time of PRPS and voltage and current values. Therefore, it was sufficient to use only asbestos separator without any additives. In further experiments, 0.8 mm thick asbestos separator was applied. Further reduction of separator thickness was impossible due to the fact that the operation time of PRPS was reduced. The reason is that thin separator became unfit because of high temperature impact.

3.2. Study of characteristics of PRPS based on magnesium

The following step of the research was the study of working characteristics of PRPS based on magnesium. Authors obtained experimental data on dependence of current and voltage on time on this stage.

It should be noted that in this study the research was performed with single cells, that in its turn significantly affects the value of current and voltage.

Experiments were conducted using the asbestos separator with thickness of 0.8 mm. With the help of experimental video storyboarding the data on duration of operation mode, as well as electrical current and voltage of PRPS were obtained (Table 3).

Table 3
Changing of the voltage and electric current during the operation mode of PRPS using separator with a thickness of 0.8 mm

Value of the electric current (A)	Value of voltage (V)	Value of duration of PRPS operation mode (sec)
0.35	0.53	2
0.85	1.30	3
0.48	0.72	4
0.43	0.65	6
0.40	0.60	8
0.38	0.57	9
0.30	0.45	12
0.10	0.15	14
0.02	0.03	600

The resulting data of storyboarding of experimental video shown in Table 3 are typical for all types of PRPS. There is a maximum of values of electric current and voltage with duration of operation mode of PRPS for a few seconds, in this case this maximum is 0.85 A during 3 sec and then it followed by major operation mode which is 0.02 A for 600 sec.

The dependence of electric current and voltage of PRPS on parameter of time is shown on Fig. 6.

On Fig. 6 (a) and (b) the rapid increase of values of electric current and voltage during first 3 sec can be observed. This phenomenon may be explained by existing of self-accelerating reaction after which the PRPS system starts the major operation mode. The important role also plays the internal resistance of

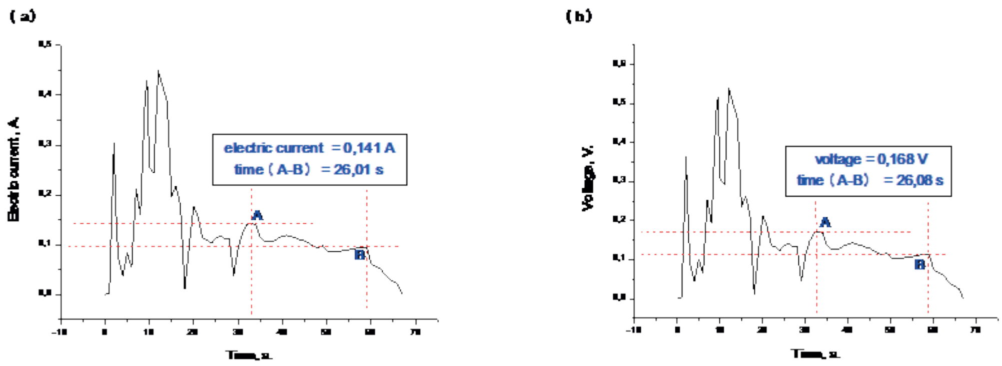

Fig. 6. The time dependence of electric current (a) and voltage (b) of PRPS.

materials, which undoubtedly contributes the value of the voltage. The internal resistance was not measured in this research.

Authors of paper [12] also measured the operation mode of PRPS based on magnesium, but the resulting voltage was 0.2 V. The duration of operation in such mode was 2–4 sec while in this research the voltage is 0.5 V and the duration of operation in such mode is close to 10 sec.

3.3 Study of characteristics of PRPS based in zinc

The final stage of this research was the investigation of characteristics of PRPS based on zinc: powder and granular zinc were used.

The experimental on investigation of characteristics of PRPS based on zinc were conducted using powder (dispersity is 65 microns) and granular (dispersity is close to 500 microns) zinc. The data on electric current and voltage which were obtained after the storyboarding of video are shown in Table 4.

The data in Table 4 shows that the maximum values of electric current and voltage using the powder of zinc are lower than the values of PRPS based on granular zinc, but the duration of stable operating mode is greater. The dependence of electric current value on parameter of time for powder and granular zinc is shown on Fig. 7.

Table 4
Values of voltage and electric current of PRPS based on zinc

Experiment	Electric current(A)	Voltage (V)
1. Zn (granular)	0.188	0.2148
2. Zn (granular)	0.201	0.2210
3. Zn (granular)	0.198	0.2300
4. Zn (powder)	0.120	0.1000
5. Zn (powder)	0.110	0.1200
6. Zn (powder)	0.090	0.1100

Figure 7 indicates that the time of increase of the value of electric current in both cases is about 100 seconds, and the maximum value of electric current for PRPS based on zinc powder is 1.2 A (Fig. 6a), whereas the granulated is 0.2 A. The explanation of this difference is that the particulate zinc has a higher surface energy and existing electrochemical reaction is more stable.

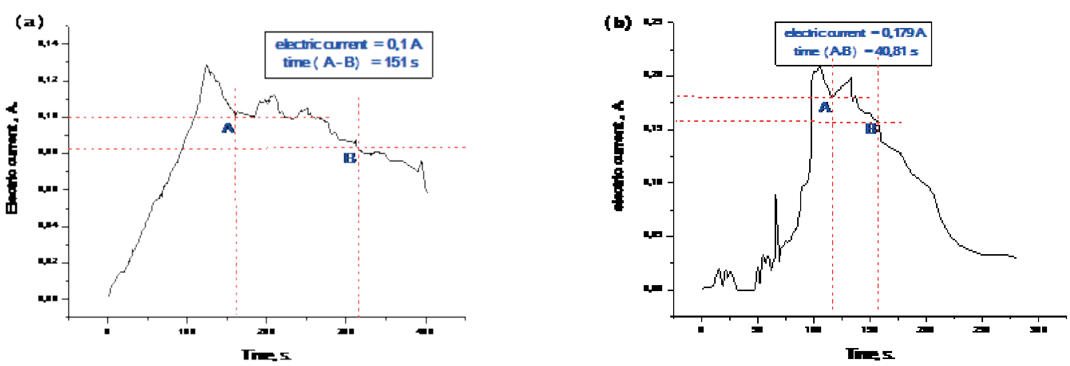

Fig. 7. The time dependence of electric current values for powder (a) and granular (b) zinc.

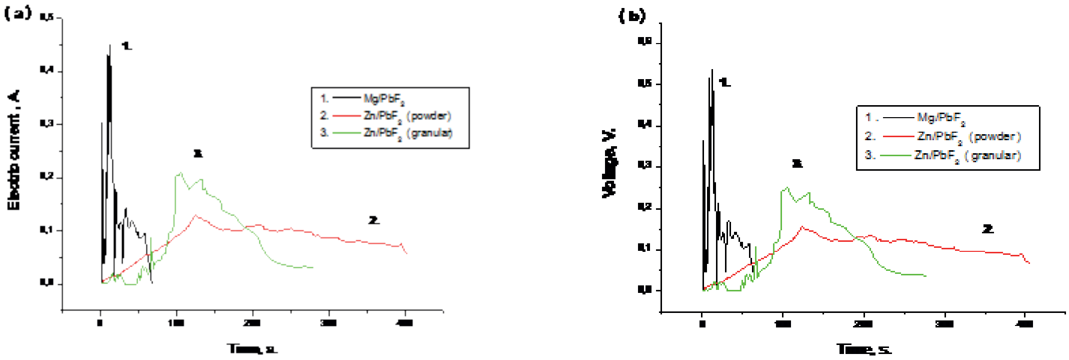

Fig. 8. The comparison of values of electric current and voltage in different systems of PRPS.

The values of electric current using powder and granular zinc are 0.179 and 0.1 A, respectively, and the duration of the operation in this mode is 40 and 151 sec, respectively. Authors of article [13] has conducted experiments on sources of electric current based on zinc with maximum value of 0.5 V. But authors [13] used cells with material weight of 50 g, while authors of this research used 10 g as a weight of cathode and anode (weight of cell is 20 g).

Based on obtained experimental data the comparative analysis was made. Figure 8 shows the comparison of the dependences of values of electric current and voltage versus time for different systems of PRPS based on magnesium, powder zinc and granular zinc.

The research has shown that while using zinc, such characteristics as the value of time to reach the operating mode, the duration of operating mode of PRPS are much higher comparing with PRPS systems based on magnesium, what also can be seen on Figs. 6 (a, b) and 7 (a, b).

Also the X-ray analyses of PRPS after the reaction was conducted and presented on Fig. 9 (a) and (b).

Based on the results of X-ray analyses it is allowed to make a several conclusions: Fig. 9 (a), we see that only 47% of magnesium takes part in electrochemical reaction, the rest part reacts with lead, and that's adversely affects the operating characteristics of PRPS thus not only preventing the formation of electrons but also overflow of charges through the separator. Figure 9 (b), about 70% zinc takes part in the electrochemical reaction, thereby increasing the operation stability and working mode of PRPS.

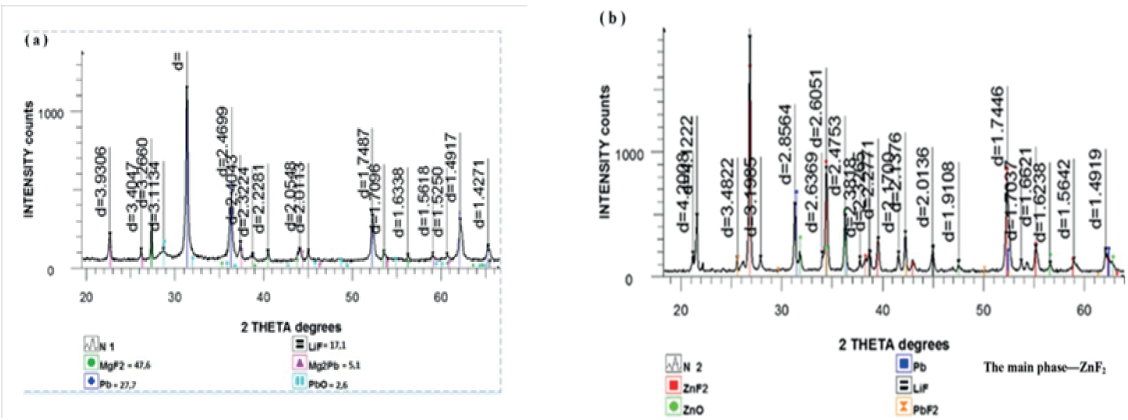

Fig. 9. X-ray analyses of PRPS with magnesium (a) and with zinc (b).

4. Conclusion

The studies revealed the influence of asbestos separator thickness on operating characteristics of the PRPS system. Based on obtained experimental data it can be concluded that with decreasing of thickness of asbestos separator the value of electric current increases. This phenomenon is obviously exists due to the fact that the increased thickness of the separator prevents the free passage of charged particles which were produced during the electrochemical reaction. The operating parameters (electric cur rent, voltage and duration of operating process of a single galvanic cell) of PRPS based on magnesium with asbestos separator with thickness of 0.8 mm were studied. Furthermore, it was found that at the value of the electric current of 0.02 A the operating time of PRPS is 585 sec.

It is found that PRPS systems based on zinc are stable during the operation process, such characteristics as the value of time-to-work, the duration of operating mode of PRPS are much higher comparing with PRPS systems based on magnesium. The electric current value using powder of zinc and granular zinc in these experiments was 0.179 A and 0.1 A, respectively, and the operating time at these values of elecrtic current was 40 and 151 sec, respectively.

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