Asian Journal of Chemistry Vol. 18, No. 2 (2006), 1199–1211

Effect of the Pyrotechnic Disc on the Efficiency of the Thermal Cell

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The effect of the composition of the assembled pyrotechnic disc upon the efficiency of the thermal cell was investigated by using mixtures of different percentages of the fuel, Fe and the oxidizing agent. In addition, the effect of the activating fuels including Mg, Al and Zr has also been studied. The results showed that, in the absence of the activating fuel, the mixture composed of 88% Fe and 12% $KClO_4$ was the most active, where it gave a voltage of 1.82 V at 58 s. This result is referred to the increment in the thermal disc glow, which gave the least heat content leading to the high voltage, 1.82 V. The results also demonstrate that using activating fuels such as Mg, Al or Zr led to some slight explosions and detonations, which gave rise to irregularity of the disc ignition. Among these, Zr was found to be the best. Extended study of different mixtures composing the assembled pyrotechnic discs, that is, 85–89% Fe and variable proportions of $KClO_4$ and Zr, disclosed that a mixture containing Fe 88%, $KClO_4$ 10% and Zr 2% was the most favourable one, which led to a glow time of 5 s. The voltage was found to be 2.27–2.30 V at 128–130 s, which was 1.82 V at 58 s, in the absence of Zr. The thermal scanning of the mixture revealed that the mixture had the heat content and entropy at 302.6°C of 10.452 $J.g^{-1}$ and 0.0180 $J.g.K^{-1}$, respectively. These results were obtained to be very close to that observed with the imported pyrotechnic disc, where the heat content and entropy at 305.88°C were 10.423 $J.g^{-1}$ and 0.0181 $J.g.K^{-1}$, respectively.

Key Words: Primary batteries, Efficiency, Thermal cell, Pyrotechnic disc.

INTRODUCTION

A thermal battery is a primary battery that is designed to be cycled (fully discharged) only once and then discarded. It is activated by heating to melt the solid electrolyte to supply electrical power for a limited time. Thermal batteries are highly trustworthy energy sources with high power densities and long shelf lives. They were nominated to be ideal for providing short-term power in expendable weapons such as projectiles, bombs, mines, missiles, rockets, torpedoes and for emergency-power circumstances such as those in the submarines and exploratory spacecrafts[1].

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Previous studies[2-4] investigated the effects of the composition of the electrodes, the temperature and the external resistance on the efficiency of the thermal cell. In the first study[2], the effect of the composition of the electrodes on the efficiency of the thermal cell has been investigated, where an efficient high temperature molten salt thermal cell has been constructed. The second study[3], which considers the temperature effect, demonstrated that the operational temperature of the laboratory thermal cell was found to be within the range 455–460°C, at which the alloy, $CaLi_2$, was formed, giving rise to the oxidation of the calcium anode and the release of the electrons. The third study[4] investigated the effect of the external resistance upon the efficiency of the thermal cell, using resistances of the range 1–1800 ohms. The results revealed that the 1800 ohms resistance proved to be the best because of giving steady discharge beside the longest period for the consumption of the cell, which approached 65 s. The passing current across the resistance was of 0.44 mA, whereas the voltage for the closed circuit was 0.62 V, which was the highest value with the lowest current, compared with the other resistances.

Concerning the pyrotechnic heat source, it is a mechanical mixture of two or more compounds, which burns without flame evolving large amount of heat. The mechanism of the pyrotechnic mixture action depends upon its components, the fuel and the oxidizer. The other additives are utilized to minimize the sensitivity and friction as well as increasing the stability. The oxidizer, which is an inorganic salt is regarded to be the main component due to the desired properties, such as, it is chemically stable, non-hygroscopic, low poisonous, its melting point ≥ 600°C, has a lot of oxygen and evolves O_2 easily. Beside the oxidizer, the fuel is considered to be one of the main components of the fire mixture. The fuel is an organic or inorganic material, which exists as metal powders or alloys, which have high thermal values. These materials are oxidized by ignition, with the aid of the oxidizer or the atmospheric oxygen[5, 6].

Selection of the fuel requires awareness about its chemical and physical properties as well as the ignition products[7]. Some of the fuels are very easily oxidized and very sensitive to collision and friction; therefore they are not utilized in some weapons[8]. To fabricate the fire mixture, some properties of the chosen fuel should be taken into consideration[9], *e.g.*, easily oxidized, ignites with use of minimum amount of oxygen beside the formation of compounds which provide the adequate effect for the fire mixture, has proper combustion heat to affect the fire mixture, chemically stable at high temperatures, having low toxicity and not highly hygroscopic.

The most important pyrotechnic heat sources used to activate the thermal cell are powders of $ZrCrO_4$ and $BaCrO_4$, Fe with Mg or Al powders or $KClO_4$[10]. The thermite mixtures are used either as a paper or compressed thermal disc[11]. The thermal paper is manufactured by employing a fire mixture of Zr with $BaCrO_4$ in specific and adequate proportions beside the additives such as ceramic and asbestos[12]. The thermal paper has a high combustion rate, great heat content which approaches 1675 $J.g^{-1}$ and ignited to give inorganic ash, which has a high electric resistance. Therefore, electrode collectors such as Ni or Fe and connectors among

the cells should be added. Hence, the current will approach the thermal paper base in the thermal cell.

A number of different systems used to activate the thermal cells at low temperatures are utilized in the thermal sensation such as detection of fire sources by affording the energy required in the communication or alert systems[13]. Many thermal cells such as

$$Ca \mid LiCl\text{-}KCl\text{-}LiNO_3 \mid MgO\text{-}Ni \quad \text{and} \quad Ca \mid LiCl\text{-}KCl\text{-}LiNO_3 \mid Ag_2CrO_4\text{-}Ni$$

which are activated at 163–232°C, were found to be suitable for the thermal sensation. In addition, an auto activated pyrotechnic source at a previously specified temperature to let the electrochemical system within the desired range of temperatures is utilized[14]. The slow heating of the pyrotechnic powders used in the traditional thermal batteries does not lead to the ignition within this range of temperature. The developed thermal generator is used in the activation of such cells, where the heat is evolved from alloying Li with the Pb-Sn solder. This alloy melts with Li at 180°C to release instantaneously the energy needed for the cell operation[15].

The object of this project was to investigate the composition of the pyrotechnic disc, that is, the fuel material such as Fe, Mg and Al and the oxidizing substance including $BaCrO_4$ and $KClO_4$ upon the efficiency of the thermal cell. The cell was composed of Ca or Mg as the anode, whereas the cathode was produced by blending the three components: $CaCrO_4$, K_2CrO_4 or $K_2Cr_2O_7$ as the depolarizer (D), LiCl-KCl eutectic mixture as the electrolyte (E) and SiO_2 as the binder.

EXPERIMENTAL

All chemicals were purchased from BDH, E. Merck or Fluka, with purities < 95%. Preparation of the molten salts as well as storing the components of the thermal cell were conducted inside a dry box flushed with argon.

The thermal analysis: The thermal behaviour for the components of the pyrotechnic disc was studied by using differential scanning calorimeter, Model DSC_7, controlled by the computer PE 7500. This instrument can differentiate and analyze the thermal properties of the materials. It is programmed under the control of the computer from the initial temperature to the final temperature *via* the transformations such as the melting, solid-solid or crystallization. The theory of the instrument running depends upon the DSC Perkin-Elmer rule for equivalent zero equilibrium. According to this rule, the energy achieved by the sample or that released by it is substituted by the addition of equivalent amount of electrical energy to the heater fastened to the sample holder or the subtraction of it. A resistance heater made of platinum beside the thermometers was used to perform the measurement of temperature and energy. The continuous automatic adjustment of the heater power was necessary to maintain the temperature of the sample to be identical with that for the support or comparison holder. This adjustment gave a variable electrical signal, which is equivalent to the variable thermal behaviour of the sample. The measurement unit was mW, which gave real electrical energy measurement for the maximum fields. For standard running, the

DSC was provided with isolated reservoir permitting the use of cold water. Therefore, the DSC could be run within the required thermal range, where a supplemented part, which circulates the water, was used[1].

Selection of the thermal cell: To be aware of the thermal cell components and their dimensions, the thermal battery, T-BO_4, was selected and cut horizontally from the electrical connection region by using rotating electrical machine. The components of the cell were identified by the X-ray diffraction. The components, dimensions were invested in the self-made cell production, profiteering the local market facilities.

Industrialization of moulds: After measuring the surface area, thickness, external and internal diameters for the anode, cathode, nickel disc and insulating asbestos disc, the mould of each component of the cell was manufactured.

Industrialization of the cell container: For the test of the self-made thermal cell, a little container was manufactured. It comprised of two interfered lids. The connection wires were passed through one lid to the voltmeter *via* very little holes, whereas the other lid contained the ignition head, attached to the pyrotechnic, which activates the electrolyte.

Production of the electrolyte disc: The electrolyte disc was produced according to the following steps:

(a.) Introducing the salts bottles into the big dry box devoted for the production.

(b.) Evacuating the dry box from air, which was replaced with argon.

(c.) Weighing the appropriate weight percentages, for the electrolyte KCl-LiCl, depolarizer $CaCrO_4$ and the binder SiO_2, which presented the optimum conditions for the laboratory thermal cell to work properly. Electronic balance, brought inside the box, was utilized.

(d.) Mixing the salts and the depolarizer thoroughly, putting them into a crucible which was covered and transferred into the furnace at 250–300°C.

(e.) Raising the temperature gradually to 620–630°C, where the mixture was completely molten. The temperature was decreased to 500°C. Hereafter, the crucible was taken out to be put inside the dry box evacuated from air and refilled with argon.

(f.) The molten salts were crushed to a very fine powder which was sieved with a 40 μm diameter sieve. The mixture was kept in a perfectly stoppered bottle.

(g.) Weighing 400 mg of the mixture, which was kept inside the electrolyte disc mould. The mould was moved to the compressor to be pressed to the desired thickness.

(h.) The electrolytic disc was laid in a perfectly stoppered bottle kept in the desiccator.

Production of the calcium disc: The calcium disc has been produced by transferring the bottle which contained calcium granules into the production dry box, which was already evacuated and refilled with argon. Thereafter, 130 g of the granules was put in the mould specified for calcium disc, followed by a proper pressing process. The produced calcium disk was kept in a thoroughly stoppered bottle.

Cutting the nickel discs: Nickel discs were cut according to the standards taken from the imported disc and laid in the desiccator.

Production of asbestos discs: Large and little asbestos discs were produced by means of the proper thermal disc moulds. Production of the little disc was carried out by drying asbestos (333 mg) at 500°C to be compressed. Asbestos (750 mg) was used for the large disc by following the same procedure. The discs were kept at 50°C inside the desiccator.

Production of the pyrotechnic disc: The pyrotechnic disc was prepared from an oxidizer such as $KClO_4$, $BaCrO_4$ or $KClO_3$, and an appropriate fuel, for instance, fine powder of Fe, Mg, Al or Zr. $KClO_4$. Fe and Zr were selected for the production of the disc. The enthalpy and the ignition temperature of the mixture were established *via* utilizing the differential scanning calorimeter (DSC). The production process was carried out by drying the oxidizer and the fuel at 50°C, where the oxidizer and the fuel were sieved with 40 μm sieve, followed by mixing the appropriate weight percentages of both. The best proper mixed percentages were accomplished by utilizing the differential scanning calorimeter instrument and pressed by the specified mould. The produced disc was laid inside the desiccator.

RESULTS AND DISCUSSION

Production of the pyrotechnic disc

Table-1 represents different weight percentages for the mixture components, that is, Fe as a fuel and $KClO_4$ as an oxidant. This mixture is considered one of the most used stable mixtures. This advantage was proved by the disadvantages encountered by using other oxidants, such as $BaCrO_4$ and $KClO_3$ and fuels, for instance Mg and Al. Mixing $BaCrO_4$ or $KClO_3$ with the fuel in the pyrotechnic mixtures led to an explosion. Likewise, employing fuels such as Mg and Ca, which widely used in the industrialization of the activating materials of the thermal batteries, are very sensitive. Hence, their utilization needs sufficient information to produce such activating materials.

Choosing of Fe and $KClO_4$ in our work was compatible with that published about their employment in the production of the thermal discs, where the weight percentages of Fe exceed 80%[16].

Table-1 reveals that the pressed mixed percentages gave divergent values for the voltage and its appearance time. It is clear that the high percentages of $KClO_4$ oxidized Fe very rapidly, retarding the glow of the mixture for a period which permits the operation of the thermal cell. In addition, it is noticed that the smaller the oxidizer percentage the greater the produced voltage. For instance, the 79% Fe and 21% $KClO_4$ gave a voltage of 0.03 V within just 3 s. This voltage increases slightly until the percentages 84% Fe and 16% $KClO_4$, where the voltage became 0.26 V at 13 s, respectively. Thereafter, at 85% Fe and 15% $KClO_4$, the voltage goes up to reach 1.04 V at 15 s. After that, the percentages 86% Fe and 14% $KClO_4$ offered 1.11 V at 20 s, whereas 87% Fe and 13% $KClO_4$, gave 1.55 V at 28 s. This result can be referred to the increase in the glow of the thermal disc which leads to a lower thermal content that ascends the voltage value.

The mixture of 88% Fe and 12% $KClO_4$ provides a voltage of 1.82 V within 58 s. After that, the voltage goes down to 1.46 V at 35 s, for 89% Fe and 11% $KClO_4$. This decrease in the voltage is due to the decrease in the oxidizer percentage which affects the glow of the thermal disc. This reasoning was proved by testing the efficiency of these discs *via* their ignition after pressing to see the glow extent. To increase the glow period for the thermal disc, other fuels such as Mg, Al and Zr, which as we mentioned before are involved in the industrialization of the activating materials, were added to the thermal disc mixture. The disc was then tested by ignition. It was demonstrated that the usage of Mg, Al causes simple explosions and detonation inside the disc, leading to irregular ignition of the disc. However, Zr has proved to be more suitable, where it was mixed with different percentages of the mixture, 88% Fe and 12% $KClO_4$. A percentage of 2% Zr was the most efficient, after the press of the disc and a very remarkable improvement of the voltage occurred. The voltage became 2.27–2.30 V *via* a time of 125–130 s. Zr characteristics such as the high stability in the pyrotechnic mixtures and corrosion-resistance qualify it to be employed in this field[17]. The effect of the addition of different percentages of Zr to the taken percentages of Fe and $KClO_4$, starting with 85% Fe and 15% $KClO_4$ up to 89% Fe and 11% $KClO_4$, has been studied. These percentages were active in the production of the voltage.

TABLE-1
EFFECT OF THE WEIGHT PERCENTAGES FOR Fe AND $KClO_4$ ON THE VOLTAGE PRODUCED AND TIME

Weight percentage for Fe (%)	Weight percentage for $KClO_4$ (%)	Voltage produced (volt)	Time (s)
79	21	0.03	3
80	20	0.07	4
81	19	0.09	6
82	18	0.11	10
83	17	0.16	11
84	16	0.26	13
85	15	1.04	15
86	14	1.11	20
87	13	1.55	28
88	12	1.82	58
89	11	1.46	35
90	10	1.01	23

Table-2 demonstrates that a mixture containing 85% Fe and different percentages of $KClO_4$ and Zr, affects highly the performance of the thermal disc. A mixture of 85% Fe, 11% $KClO_4$ and 4% Zr gave a glow time of 3 s, whereas a mixture containing 1% Zr and 14% $KClO_4$ offered a momentary glow time and

a mixture of 2% Zr and 13% $KClO_4$ gave a 1 s glow time. At 3% Zr and 12% $KClO_4$, the glow time was 2 s, which descended to 1 s at 5% Zr to become weakly ignited at 6% Zr. In addition, the table demonstrated that increasing the Fe percentage to 85% and lowering the Zr percentage have obvious effect upon the performance of the thermal disc.

TABLE-2
THE DISC GLOW TIME OBTAINED WITH THE MIXED VARIABLE PERCENTAGES OF $KClO_4$ AND Zr AND INVARIABLE 85% Fe

Weight percentage of $KClO_4$ (%)	Weight percentage of Zr (%)	Glow time of the disc (s)
14	1	Momentary
13	2	1
12	3	2
11	4	3
10	5	1
9	6	Weakly ignited

Differential scanning calorimeter demonstrated that the mixture composed of 85% Fe, 11% $KClO_4$ and 4% Zr had a heat content of 12.57 $J.g^{-1}$ for a 7 mg sample, whereas the entropy was 0.021 $J.g.K^{-1}$ as concluded from Fig. 1. The same figure shows that running the thermal cell in the existence of 4% Zr presented a voltage of 1.18 V within 25 s. However, in the absence of Zr, the voltage was 1.04 V with a time of 15 s.

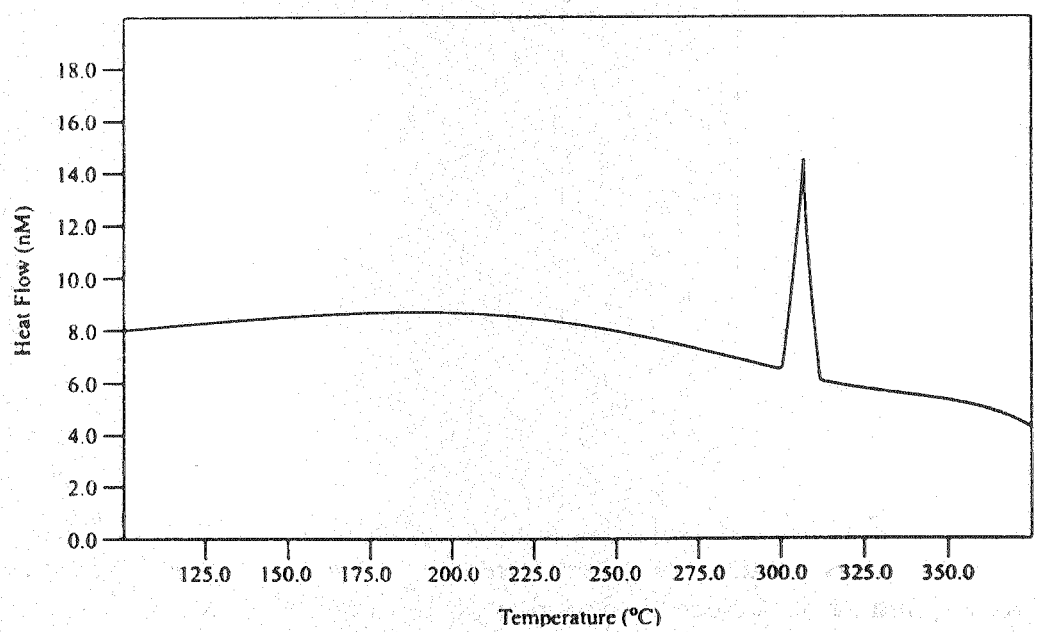

Fig. 1. Thermal scanning for the thermal disc composed of 85% Fe, 11% $KClO_4$ and 4% Zr

Table-3 demonstrates the glow time for each of the mixtures containing 86% Fe and different percentages of $KClO_4$ and Zr. It is clear that 11% $KClO_4$ and

3% Zr gave the highest glow time of 3 s, which was 2 s with 4% Zr. Table-3 also reveals that 2% Zr gave a glow time of 2 s whereas 1% Zr offered 1 s time. Moreover, the disc became weak ignitable at 5% and 6% Zr.

Fig. 2 illustrates the thermal scanning for the mixture composed of 86% Fe, 11% $KClO_4$ and 3% Zr. The figure demonstrates that the enthalpy became 11.851 $J.g^{-1}$ while the entropy was 0.02 $J.g.K^{-1}$, which confirms the increment of the order of the molecules with increasing the percentage of Fe. The cell running with this disc, gave a voltage of 1.31 V within a 25 s time. However, in the absence of Zr, the voltage was 1.11 V with a time of 20 s.

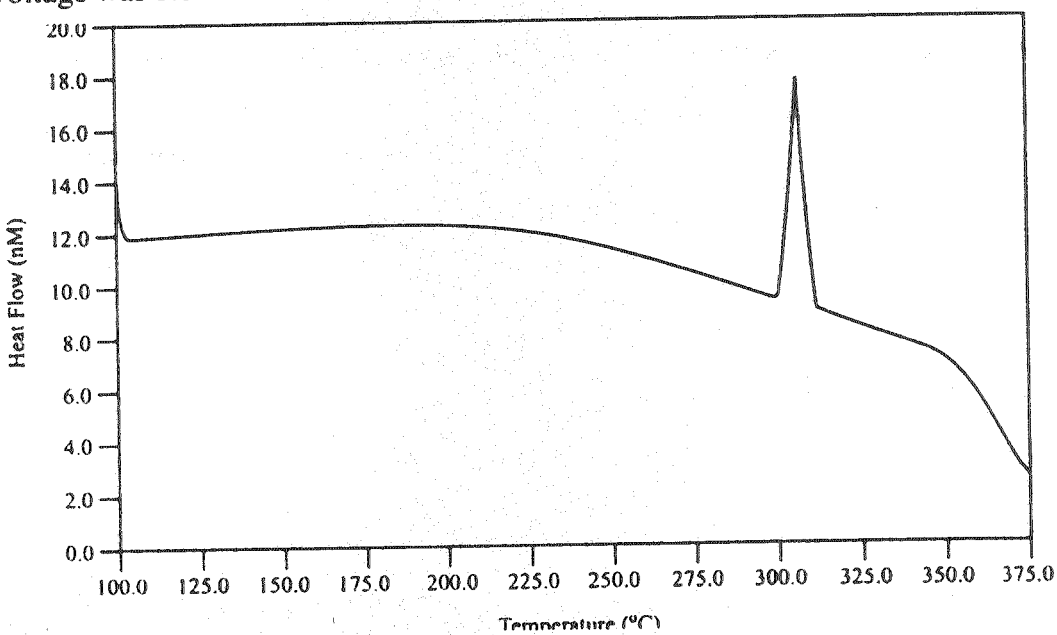

Fig. 2. Thermal scanning for the thermal disc composed of 86% Fe, 11% $KClO_4$ and 3% Zr

TABLE-3
THE DISC GLOW TIME OBTAINED WITH THE MIXED VARIABLE PERCENTAGES OF $KClO_4$ AND Zr AND INVARIABLE 86% Fe

Weight percentage of Zr (%)	Weight percentage of Zr (%)	Glow time of the disc (s)
13	1	1
12	2	2
11	3	3
10	4	1
9	5	Weakly ignited
8	6	Weakly ignited

Table-4 shows the data for the mixture of 87% Fe and different percentages of $KClO_4$ and Zr. It is clear that the mixture containing 11% $KClO_4$ and 2% Zr was the best, indicating that the 2% Zr promoted the disc activity affording a glow time of 4 s and a voltage of 1.73 V with an operation period of 50 s. However, in the absence of Zr, the voltage and the time were 1.55 V and 28 s, respectively. A marked improvement of the voltage took place with the high

percentage of Fe, *i.e.*, 87%. The enthalpy for the mixture was 10.521 $J.g^{-1}$ with an entropy of 0.0181 $J.g.K^{-1}$. With 1% Zr and 3% Zr, the glow time was 2 s. In the case of 5% Zr and 6% Zr the disc became weakly ignitable.

Fig. 3 reveals the thermal scanning for the mixture composed of 87% Fe, 11% $KClO_4$ and 2% Zr, demonstrating that the thermal content for this mixture is 10.521 $J.g^{-1}$ whereas the entropy is 0.081 $J.g.K^{-1}$.

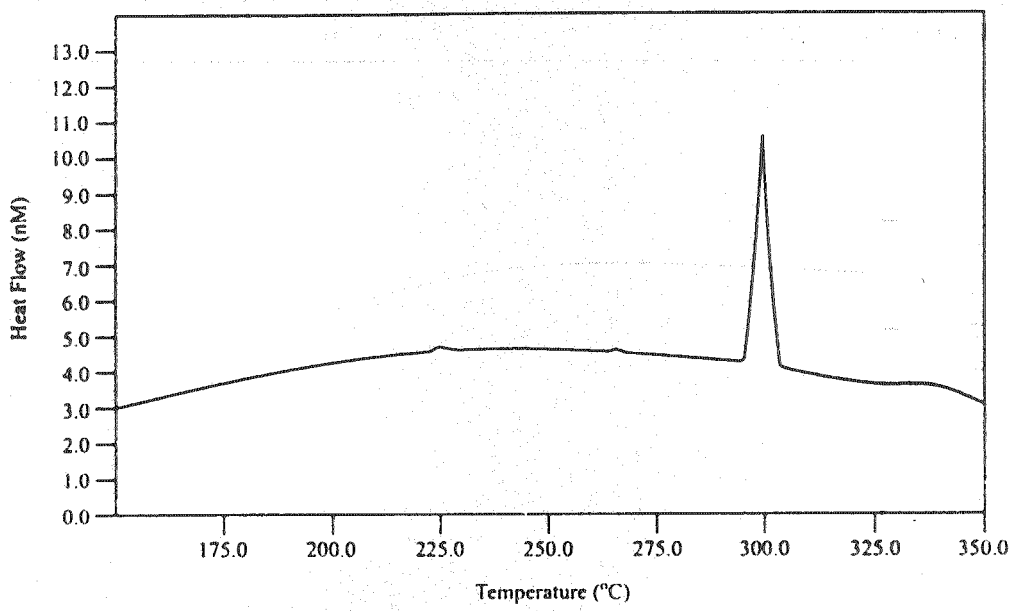

Fig. 3. Thermal scanning for the thermal disc composed of 87% Fe, 11% $KClO_4$ and 2% Zr

TABLE-4
DISC GLOW TIME OBTAINED WITH THE MIXED VARIABLE PERCENTAGES OF $KClO_4$ AND Zr AND INVARIABLE 87% Fe

Weight percentage of $KClO_4$ (%)	Weight percentage of Zr (%)	Dlow time of the disc (s)
12	1	2
11	2	4
10	3	2
9	4	1
8	5	Weakly ignited
7	6	Weakly ignited

Table-5 shows the data for the mixture composed of 88% Fe and different percentages of $KClO_4$ and Zr. It demonstrates that the percentages 10% $KClO_4$ and 2% Zr was very active in the production of the thermal cell, where the glow time was 5 s. For 1% Zr the glow time was 2 s. However, the disc was weakly ignited for the percentages 4, 5 and 6% Zr. Moreover, there was a significant alteration upon the cell voltage and the accompanied time, where the voltage and its time changed from 1.82 V and 58 s, in the absence of Zr to 2.7–2.3 V and 130 s when Zr was added.

Fig. 4 shows the thermal scanning for the mixture composed of 88% Fe, 10% $KClO_4$ and 2% Zr. It reveals that the enthalpy and the entropy and the peak area are 10.452 $J.g^{-1}$, 0.018 $J.g.K^{-1}$ and 73.160 mJ, respectively. These percentages for the disc gave very similar results to that noticed are shown in Fig. 5. The figure illustrates the values of the heat content and entropy, which are 10.423 $J.g^{-1}$ and 0.0181 $J.g.K^{-1}$, respectively. The peak temperatures for the imported and laboratory discs were 305.88 and 302.6°C, respectively. Another better comparison can be accomplished in the existence of sieves of size less than 40 μm.

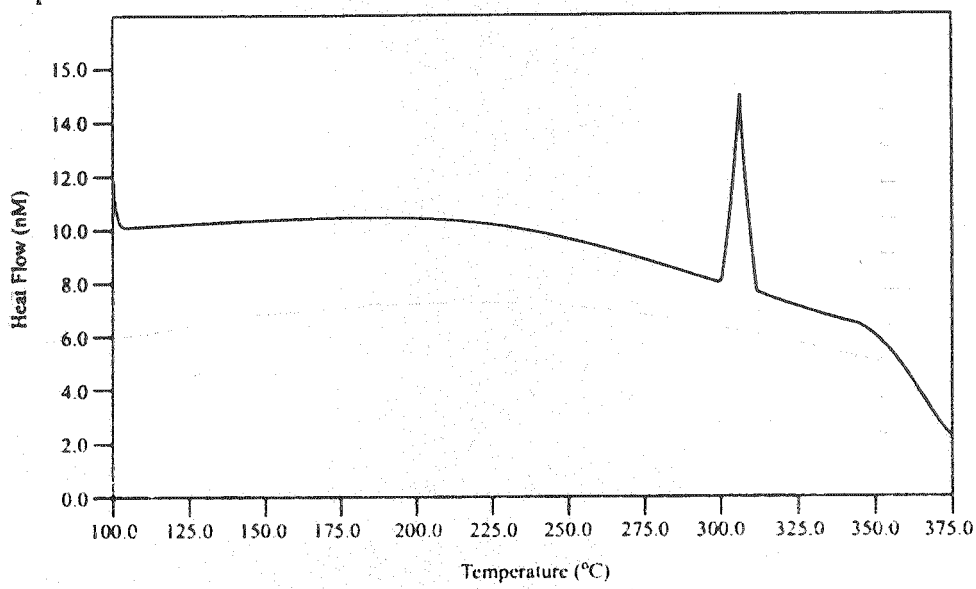

Fig. 4. Thermal scanning for the thermal disc composed of 88% Fe, 10% $KClO_4$ and 2% Zr

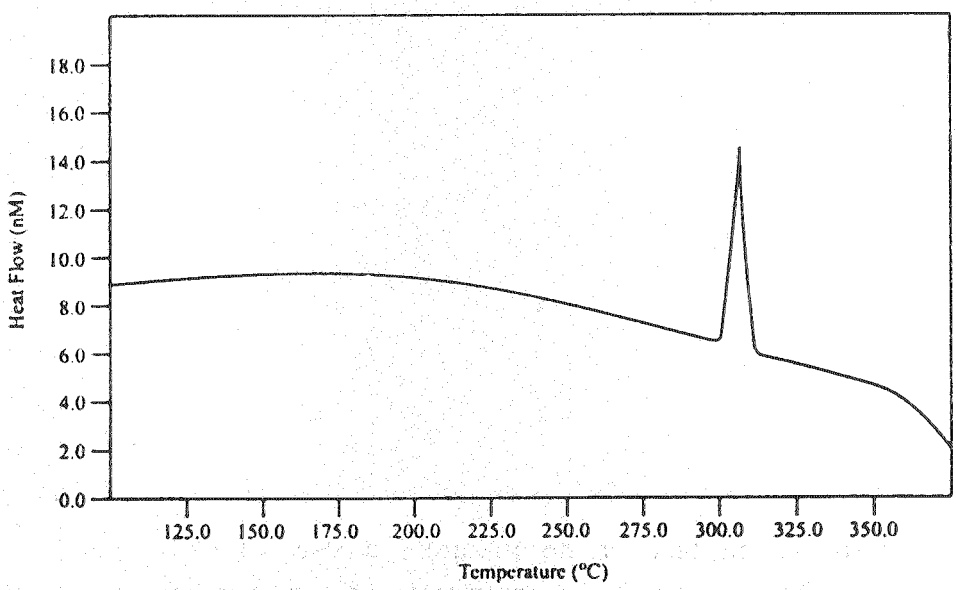

Fig. 5. Thermal scanning for the imported thermal disc

Table-6 illustrates the data for the 89% Fe and different percentages of $KClO_4$ and Zr. The results proved that the best percentage was 10% $KClO_4$ and 1% Zr, which gave a glow time of 3 s, was active but with a less voltage and time, compared with the mixture of 89% Fe and 11% $KClO_4$, *i.e.*, in the absence of Zr. The voltage and time for the mixtures (89% Fe, 10% $KClO_4$ and 1% Zr) and (89% Fe and 11% Zr) were 1.57 V and 65 s and 1.46 V and 35 s, respectively. This percentage can be

used in the production of a less efficient disc. The other percentages demonstrated that the mixture of 9% $KClO_4$ and 2% Zr gave a glow time of 1 s, while the ignition became weak for the percentages 5, 6, 7 and 8% of $KClO_4$ and 3, 4, 5 and 6% of Zr, respectively.

Table-6 illustrates the data for the 89% Fe and different percentages of $KClO_4$ and Zr. The results proved that the best percentage was 10% $KClO_4$ and 1% Zr, which gave a glow time of 3 s, was active but with a less voltage and time, compared with the mixture of 89% Fe and 11% $KClO_4$, *i.e.*, in the absence of Zr. The voltage and time for the mixtures (89% Fe, 10% $KClO_4$ and 1% Zr) and (89% Fe and 11% Zr) were 1.57 V and 65 s and 1.46 V and 35 s, respectively. This percentage can be used in the production of a less efficient disc. The other percentages demonstrated that the mixture of 9% $KClO_4$ and 2% Zr gave a glow time of 1 s, while the ignition became weak for the percentages 5, 6, 7 and 8% of $KClO_4$ and 3, 4, 5 and 6% of Zr, respectively.

TABLE-5
THE DISC GLOW TIME OBTAINED WITH THE MIXED VARIABLE PERCENTAGES OF $KClO_4$ AND Zr AND INVARIABLE 88% Fe

Weight percentage of $KClO_4$ (%)	Weight percentage of Zr (%)	Glow time of the disc (s)
11	1	2
10	2	5
9	3	2
8	4	Weakly ignited
7	5	Weakly ignited
6	6	Weakly ignited

Fig. 6 demonstrates that the enthalpy of the operation equals 8.913 $J.g^{-1}$ which started at 299.6°C and ended at 312.4°C to become lower than that for the previous mixture by 2 $J.g^{-1}$.

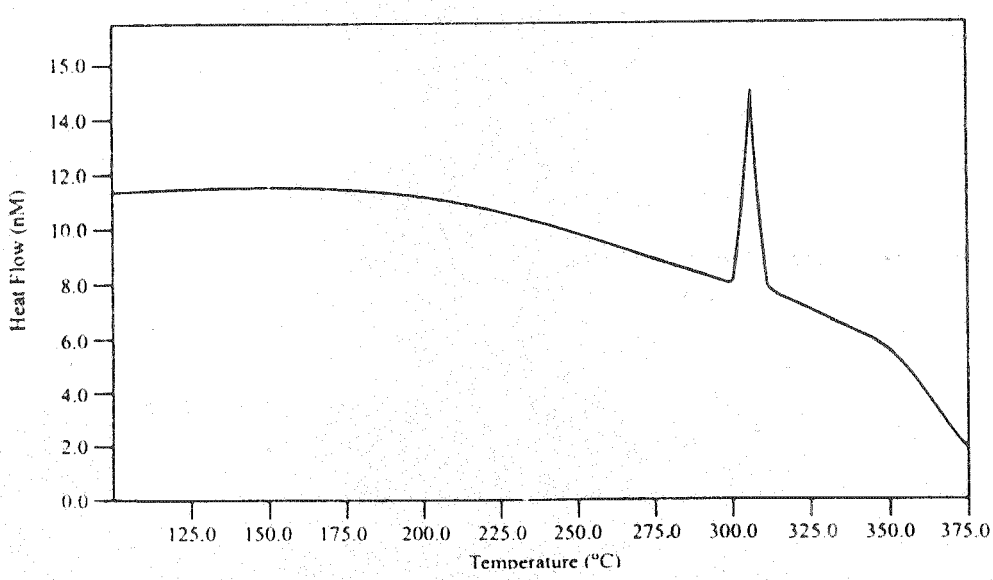

Fig. 6. Thermal scanning for the thermal disc composed of 89% Fe, 10% $KClO_4$ and 1% Zr

TABLE-6
DISC GLOW TIME OBTAINED WITH THE MIXED VARIABLE PERCENTAGES OF $KClO_4$ AND Zr AND INVARIABLE 89% Fe

Weight percentage of $KClO_4$ (%)	Weight percentage of Zr (%)	Glow time of the disc (s)
10	1	3
9	2	1
8	3	Weakly ignited
7	4	Weakly ignited
6	5	Weakly ignited
5	6	Weakly ignited

Concerning the effect of the addition of Zr to the mixed percentages of Fe and $KClO_4$, upon the voltage and time, Table-7 shows the percentages of Zr accompanied with the corresponding voltages and times.

TABLE-7
EFFECT OF Zr ADDED TO THE MIXED PERCENTAGES OF Fe AND $KClO_4$ UPON THE VOLTAGE AND TIME

Weight percentage of Fe (%)	Weight percentage of $KClO_4$ (%)	Weight percentage of Zr (%)	Produced voltage (V)	Time (s)
85	11	4	1.18	25
86	11	3	1.31	40
87	11	2	1.73	50
88	10	2	2.27–2.30	128–130
89	10	1	1.57	65

Regarding the effect of adding Zr to the mixed percentages of Fe and $KClO_4$, upon the thermodynamic parameters, Table-8 revealed the percentages of Zr accompanied with the corresponding mentioned parameters.

TABLE-8
THE EFFECT OF Zr ADDED TO THE MIXED PERCENTAGES OF Fe AND $KClO_4$ UPON SOME THERMODYNAMIC PARAMETERS

Weight percentage of Fe (%)	Weight percentage of $KClO_4$ (%)	Weight percentage of Zr (%)	ΔH ($J.g.^{-1}$)	ΔS ($J.G.K^{-1}$)
85	11	4	12.57 for 7 mg	0.0210
86	11	3	11.851	0.0200
87	11	2	10.521	0.0181
88	10	2	10.452*	0.0180†
89	10	1	8.913	

*10.423 $J.g^{-1}$ for the foreign one. †0.0181 $J.g.K^{-1}$ for the foreign one.

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(*Received*: 31 May 2005; *Accepted*: 22 December 2005) AJC-4554