

## Effect of the Composition of the Electrodes on the Efficiency of Thermal Cell

WALEED M. SARHAN†, AHMED N. ALKHATEEB‡ and FALAH H. HUSSEIN\*

Chemistry Department, College of Science for Women, Babylon University, Babylon, Iraq

E-mail: abohasan\_hilla@yahoo.com

An efficient high temperature molten salt thermal cell has been constructed, which was composed of Ca or Mg as the anode. The cathode was produced by blending the three components viz.,  $\text{CaCrO}_4$ ,  $\text{K}_2\text{CrO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  as the depolarizer (D), LiCl-KCl eutectic mixture as the electrolyte (E) and  $\text{SiO}_2$  as the binder (B). The influence of the cathode components (DEB) upon the efficiency of the thermal cell, where the anode was Ca, was investigated. It was found that the weight percentage of eutectic mixture (E): 55.2% KCl and 44.8% LiCl, gave the lowest eutectic point, namely, 355°C. In addition, the weight percentages of the depolarizer (D);  $\text{CaCrO}_4$  and the binder,  $\text{SiO}_2$  of 83% and 17%, respectively, generated the maximum produced voltage of 0.8 V at 460–465°C. However, mixtures of 75%  $\text{K}_2\text{Cr}_2\text{O}_7$  and 25%  $\text{SiO}_2$ , 30%  $\text{K}_2\text{CrO}_4$  and 70%  $\text{SiO}_2$  gave voltages of 0.41 and 0.48 volts. Using Mg anode with the same eutectic mixture, a mixture of 90%  $\text{CaCrO}_4$  and 10%  $\text{SiO}_2$ , 78%  $\text{K}_2\text{Cr}_2\text{O}_7$  and 22%  $\text{SiO}_2$  gave voltages of 0.42 and 0.44 V, respectively, indicating that Ca is more efficient than Mg. Thermal analysis study for the electrolyte in the absence of the depolarizer,  $\text{CaCrO}_4$ , using the differential scanning calorimeter (DSC) showed that the beginning of LiCl-KCl mixture eutectic point was 343°C, where the enthalpy was 23.3 J g<sup>-1</sup>. However, using  $\text{CaCrO}_4$  as a depolarizer gave a eutectic point of 380°C, where the enthalpy was 88 J g<sup>-1</sup>, which is much greater than that in the absence of the depolarizer, and hence a higher voltage, 80 V, was generated. Using  $\text{K}_2\text{Cr}_2\text{O}_7$  as a depolarizer gave a eutectic point of 299°C and enthalpy of 40 J g<sup>-1</sup>, which is half that found with  $\text{CaCrO}_4$ . In addition, usage of  $\text{K}_2\text{CrO}_4$  revealed a eutectic point of 359°C and a lesser enthalpy, that is, 20.8 J g<sup>-1</sup>, and consequently a lower voltage was produced.

### INTRODUCTION

The thermal cell was invented in 1940 and developed mainly for launching missiles<sup>1</sup>. A serial-connection of these cells gives the thermal battery. The design of the thermal battery depends upon the desired performance specifications<sup>2</sup>. Thermal batteries have rugged construction, long storage life and require no maintenance. Consequently, they are most often used for military applications such as rockets, bombs, torpedoes, missiles, mines, decoys and for emergency-power systems such as those in submarines or aircrafts<sup>3</sup>. Molten inorganic salts are used in the thermal batteries as electrolytes, which are solid non-conducting

†Chemistry Department, College of Science, Kufa University, Iraq.

‡Chemistry Department, College of Science, Ibb University, Yemen.

at ambient temperatures. An energy pulse from an external source activates the battery and ignites the pyrotechnic materials within the battery to melt the electrolyte, which becomes an ionic conductor. Thus, electricity is generated electrochemically for periods ranging from a few seconds to an hour<sup>4</sup>. Depending upon its composition, a thermal battery can generate voltages of 1.5–3.3 volts.

Configuration of the battery cells is composed of an anode, electrolyte, cathode and the pyrotechnic heat source, which connects the cells. The anode is made of alkali or earth alkali metals. Most of the thermal cell designs use Ca as an anode, which is connected to a current collector, made of iron, rust-resistance steel or Ni. Throughout the last decades, manufacturing of the anodes has been developed *via* the usage of Li metal or Li-alloys, such as Li-Si, Li-B and Li-Al, as anodes<sup>5</sup>. This development belongs to the desired characteristics of Li, namely, high standard potential (–3.04 V) and low molecular equivalent. In addition, the polarization resulting within the molten salt electrolytes is low. However, Li defects including the low melting point (180°C) and the high oxidation rate caused some problems in the manufacturing process of the thermal cells, which led to the limitation of Li usage<sup>6</sup>.

Concerning the cathode, the elements in the groups VB, VIB, VIIB of the periodic table were used<sup>7</sup>. Moreover, uppermost elements of the mentioned groups are preferred due to their low molecular equivalents<sup>8</sup>. Many materials<sup>9</sup> are used to make the cathodes such as  $K_2CrO_4$ ,  $PbCrO_4$ ,  $CaCrO_4$ ,  $CuCrO_4$ ,  $WO_3$ ,  $V_2O_5$  and  $Fe_2O_3$ . The electrolyte is a molten salt which has the characteristics: excellent electricity conductor, good solving for the products formed at the electrodes, during the thermochemical reaction and should be stable at 250°C above the melting point<sup>10</sup>. The pyrotechnic heat source is a mechanical thermite mixture of two or more compounds, which burns without flame, evolving large amount of heat<sup>11</sup>. The mechanism of the pyrotechnic mixture action depends upon its components, the fuel and the oxidizer<sup>12</sup>; the other additives act for reducing the sensitivity and friction as well as promoting the stability. The oxidizer is the main component which is an inorganic salt which has the characteristics: the melting point  $\geq 60^\circ C$ , has a lot of oxygen, evolves  $O_2$ , easily chemically stable, not highly hygroscopic and low poisonous<sup>13</sup>.

The effect of the catholyte layer processing on the thermal cell performance, where the catholyte layer is composed of three components, that is: the depolarizer (D),  $CaCrO_4$ ; the electrolyte, LiCl-KCl eutectic and the binder,  $SiO_2$ , was studied by Szwarc and Walton<sup>14</sup>. The DEB pellets, the catholyte, layer were produced *via* blending of the mentioned components, fusing, grinding the cake and hydrostatically compressing the powder into pellets. It was found that the powder processing procedure affects the capacity of the cell but not the voltage. On the other hand, an increase in the capacity was noticed by increasing the pre-bake temperature for  $CaCrO_4$  from 400–600°C. However, this system has some disadvantages resulting from a series of reactions that occur at the anode to form a liquid calcium-lithium alloy, a KCl- $CaCl_2$  double salt (m.p. 752°C) and a  $Ca_2CrO_4Cl$  layer adjacent to the anode. Hence, thermal batteries using LiCl-KCl mixtures are generally designed to operate at internal temperatures between 475 and 550°C<sup>15</sup>.

Miles *et al.*<sup>15</sup> succeeded in solving the mentioned problems encountered with the batteries, which are composed of LiCl-KCl mixture as the electrolyte, Ca as the anode and  $\text{CaCrO}_4$  as a cathodic component, by replacing LiCl-KCl with nitrate salts as a lower melting electrolyte. Using of nitrate salts reduces the activation time for the thermal cell and decreases the weight of heat sources and insulation. In addition, the nitrate also works as the cathode material or oxidizer, thus simplifying battery construction by excluding the usage of a separate oxidizer. Moreover, nitrate salts are low hazard materials, compared with other oxidizers, such as  $\text{CaCrO}_4$ , which is a well-recognized carcinogen. Single cell tests were carried out utilizing various salt mixtures containing  $\text{LiNO}_3$  and added halides. The best results were observed by utilizing a 50–25–25 mole per cent mixture of  $\text{LiNO}_3$ -LiCl-KCl. This system could be operated over a temperature range of 250–450°C to generate 2.5–2.8 V at open-circuit and initial operating voltages above 2 V at 10 mA  $\text{cm}^{-2}$ . Activated lifetimes to 75% of the peak discharge voltages are 45, 26, 21, 10 and 9 min at temperatures of 250, 300, 350, 400 and 450°C, respectively. This cell could also be activated at lower temperatures, but cell performance is poor (1.2 V at 2 mA  $\text{cm}^{-2}$  at 175°C).

The electrolyte effects in Li-alloy/ $\text{FeS}_2$  thermal batteries have been studied by Guidotti and Reinhardt<sup>16</sup>. The most common Li-alloys used for anodes are 20% Li-80% Al and 44% Li-56% Si. Liquid Li supported with iron powder was also applied. The most used electrolyte in thermal batteries was the LiCl-KCl eutectic that melts at 352°C. However, the LiCl-LiBr-LiF eutectic, which melts at 436°C, showed the best rate and power characteristics. This has been referred to the very low polarization due to the absence of Li(+) gradients familiar with the LiCl-KCl eutectic.

Styczynski *et al.*<sup>17</sup> investigated the properties of two electrochemical thermal cells, namely,  $\text{Ca} \mid \text{LiCl-KCl} \mid \text{PbSO}_4$  and  $\text{Mg} \mid \text{LiCl-KCl} \mid \text{PbSO}_4$ , and a comparison of the Ca and Mg anodes cells. The anode was made of a Ca or Mg sheet. The electrolyte was a mixture of LiCl and KCl mixture deposited on a cloth of glass fibres separator. The cathode was prepared by depositing  $\text{PbSO}_4$  on Ni wire. The study compromised a discharging of the cells by external resistances, which was altered stepwise and cyclically. Cells with Mg anodes were studied at 400–550°C, whereas with Ca anodes, at 450–650°C. The investigated cathodes with different LiCl-KCl ratios revealed that with Ca anodes, a considerable effect on the observed discharge capacity took place. However, with Mg anodes this effect was insignificant. Moreover, all the electrolyte compositions, except that with 75% KCl and 25% LiCl, led to a short-circuit of the Ca cells. With this electrolyte, Mg cells gave the highest discharge capacity.

The aim of this project was to construct a high temperature molten salt thermal cell, where the anode is Ca or Mg, whereas the active cathode material was chosen to be thermally stable at high temperatures as well as efficient in supplying high voltage. The proposed design for the cathode included the use of LiCl-KCl eutectic mixture as the electrolyte (E) because it is easily obtainable beside its high conductance at high temperatures. Another object was to evaluate the effects of different weight percentages of different depolarizers (D) and the binder (B), upon the activity of the cell. The work also aimed to investigate a comparison

between Ca and Mg anodes and studying their effects on the efficiency of the cell.

### EXPERIMENTAL

All the used chemicals were purchased from BDH, E. Merk or Fluka, with purities > 95% and were used as supplied. 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 glass cell was built in the glass workshop of the Chemistry Department, College of Science, Babylon University, Iraq. It was made by cutting a pyrex glass tube. A concavity was made with a depth of 6 mm, which could accommodate appropriate amount of solid electrolyte and the entrance of the cell electrodes to the electrolyte. In addition, another glass rod of 3 mm diameter was made, for the entrance of the connection wires from the electrodes to outside, to guarantee no contact of the wires. The cell was fastened in the furnace by a pyrex beaker, and connected to a voltmeter during the running process.

**The preparation of molten salts:** The molten salts were prepared by mixing different percentages of KCl with LiCl, and LiBr with KBr. In each case, the mixture was crushed to a powder, put in a crucible to be transferred to the furnace whose temperature had been raised from 200 to 620–630°C, where the powder melted completely to become a clear solution. Then, the furnace was switched off. When the temperature reached 500°C, the crucible was moved to the dry box. After that, the mixture, which solidified after ten minutes, was thoroughly ground to give a very fine powder of the molten KCl-LiCl. The desired electrolyte was prepared by the finding of the best weight percentage ratio of the salts *via* the determination of the best eutectic point, that is, with the lowest m.p., using the thermal cell, which was used to monitor directly the transformation of the powder to the molten phase inside the furnace.

**Determination of the weight percentage ratio for the depolarizer:** The weight percentage for the depolarizer relative to that for the binder was determined by transferring appropriate amount of the prepared molten electrolyte to the glass cell. The glass cell was placed in a beaker to be fastened in the furnace. The cell was then connected to a voltmeter and the temperature of the furnace was fixed at 200°C. Reaching the highest voltage and the time associated with it, was followed by repeating the process with different ratios of the depolarizers such as CaCrO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>4</sub> and K<sub>2</sub>CrO<sub>4</sub> and the binder, SiO<sub>2</sub>. The same process was again repeated substituting Ca with Mg. As a result, CaCrO<sub>4</sub> was selected as the proper depolarizer with the Ca anode.

**Operation of the thermal cell:** After establishing the optimum conditions for the operation of the thermal cell, the molten salts were prepared, mixed with the appropriate depolarizer and the binder, SiO<sub>2</sub>. The mixture was transferred to the glass cell. The cell was laid in the furnace and connected to the voltmeter. The temperature suitable for the cell operation was determined by raising the temperature, starting with 200°C until the temperature at which the voltage depressed to zero.

**Thermal analysis:** The thermal behavior of the electrolyte was studied by utilizing differential scanning calorimeter (DSC), model DSC<sub>7</sub>, 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<sup>18</sup>. 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 the 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 the mW, which gave real electrical energy measurement for the maximum fields. For the 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.

## RESULTS AND DISCUSSION

**The anode:** Calcium was selected to be the anode for the laboratory thermal cell due to the wide utilization of it, which provided us with some useful information concerning this electrode and its low density. Magnesium was also used because it is available and easy to deal with. However, it has some disadvantages including the shortage of the information concerned with its usage as well as being more dense than calcium.

**The cathode:** The cathode is designed to be a mixture of a depolarizer (D), electrolyte (E) and a binder (B), which is abbreviated as DEB. This design was chosen due to favourable characteristics, namely, the relative stability, low cost and the simple structure, where there is no need for separating layers of the electrolyte, binder and the depolarizer<sup>18</sup>. Moreover, the glass cell can be easily used due to the smooth operation in the absence of the multi-layers. The molten salt, the electrolyte used (E), was a mixture of KCl and LiCl because of their availability and wide use in the production of the thermal cells electrolytes. In addition, this eutectic mixture has a high electric conductivity at high temperatures<sup>19</sup>. Fig. 1 shows that the mixture of the component weight percentages, 55.2% KCl and 44.8% LiCl, gave the lowest eutectic point, namely, 355°C. The depression in the eutectic point depends, among other factors, upon the percentages of the mixture components. This depression may be attributed to the Li<sup>+</sup> ions with a small radius, which leads to a large attraction with the anions.

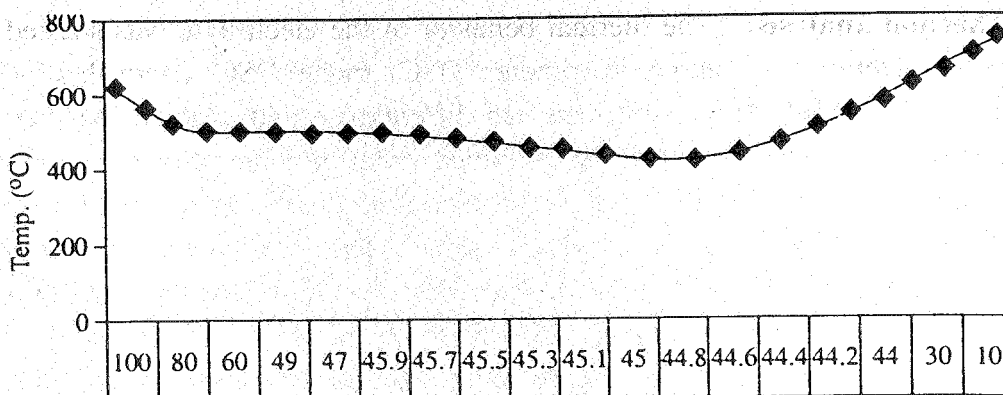


Fig. 1. Determination of the eutectic point for the mixture of LiCl-KCl

After the determination of the eutectic point for the two salts, KCl and LiCl, where  $\text{SiO}_2$  was selected to be the binder with different depolarizers, the Ca electrode was left unchanged. Fig. 2 demonstrates the relation between the weight

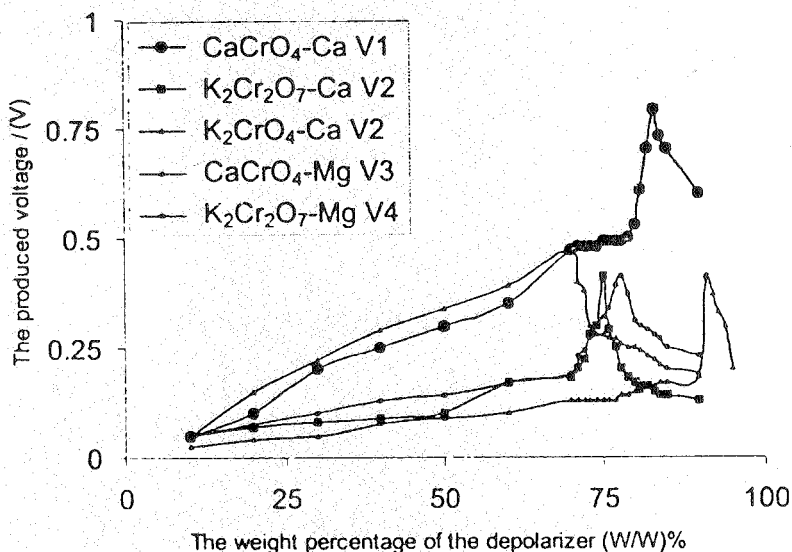


Fig. 2. The relation between the weight percentages of the depolarizers and the produced voltages

percentages of the depolarizers and the produced voltages. Different weight percentages of  $\text{SiO}_2$  and the depolarizer,  $\text{CaCrO}_4$ , were used starting with 10%  $\text{SiO}_2$  and 90%  $\text{CaCrO}_4$  until 90%  $\text{SiO}_2$  and 10%  $\text{CaCrO}_4$ . It was obtained that highest voltage, 0.8 V, at 460–5°C was reached when the mixture component weight percentages were 17%  $\text{SiO}_2$  and 83%  $\text{CaCrO}_4$ . Then, it started to depress due to the increment of the depolarizer percentage which may affect the equilibrium position of the electrochemical reaction.

However, using  $\text{K}_2\text{Cr}_2\text{O}_7$  as a depolarizer, in a mixture of 75%  $\text{K}_2\text{Cr}_2\text{O}_7$  and 25%  $\text{SiO}_2$ , lowered the produced voltage to 0.41 V. This could be referred to the low melting point and easy decomposition of  $\text{K}_2\text{Cr}_2\text{O}_7$ , which affected the operation of the cell. This explanation was confirmed by replacing  $\text{K}_2\text{Cr}_2\text{O}_7$  with  $\text{K}_2\text{CrO}_4$ . The produced voltage of 0.48 V indicated the greater stability of the  $\text{K}_2\text{CrO}_4$  compared with the dichromate.

In the case of using Mg as a cathode, the electrolyte used was KCl-LiCl. The

shortage of information about the depolarizers used with Mg necessitated the use of  $\text{CaCrO}_4$ . The best weight ratio used was 0.9  $\text{SiO}_2$  : 9.1  $\text{CaCrO}_4$  (w/w) which produced 0.42 V. Using a mixture of 78%  $\text{K}_2\text{Cr}_2\text{O}_7$  and 22%  $\text{SiO}_2$  gave a voltage of 0.44 V. However, a higher voltage may be achieved by utilizing depolarizers, which are more compatible with the Mg electrode. This expectation is based upon the fact that Mg is less sensitive to moisture than Ca.

**Thermal analysis:** A study had been carried out for the electrolyte before the operation of the glass thermal cell. The cell was examined with change of the electrodes, depolarizer and the binder. Using differential scanning calorimeter (DSC), the changes occurring in the electrolyte with increase in the temperature have been followed.

Fig. 3 reveals the behaviour of the electrolyte ( $\text{LiCl-KCl}$ ) in the absence of the depolarizer. Two peaks appear. The first one starts with 65 and terminates at  $175.733^\circ\text{C}$ , having  $\Delta H$  equal to  $352.458 \text{ J g}^{-1}$ . With rise in temperature, ascending of the curve is obtained, as a result of losing crystallization water. After  $143^\circ\text{C}$ , strong descending for the curve is noticed. This can be attributed to two processes. The first one is exothermic arising from the elimination of crystallization water. The second process, which represents the start of the melting of the sample, is endothermic. The two processes are synchronous. Then, slow gradual melting begins. After that, the curve starts ascending, which represents the beginning of the eutectic case at  $343^\circ\text{C}$ , which has enthalpy of  $23.3 \text{ J g}^{-1}$ .

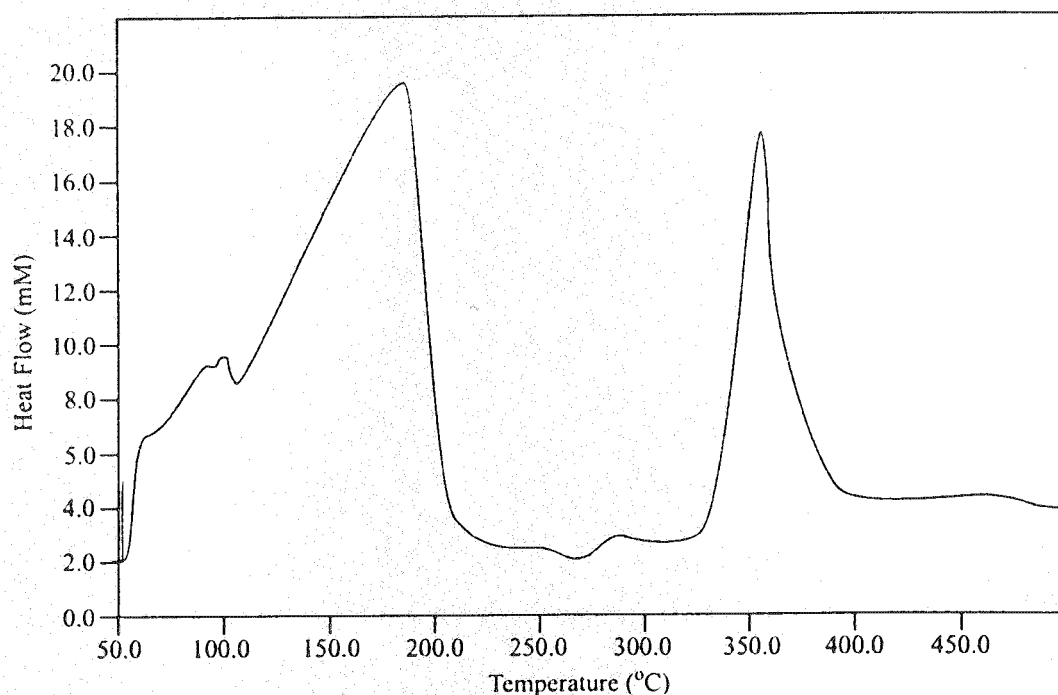


Fig. 3. The thermal behavior of the electrolyte in the absence of the depolarizer

Fig. 4 demonstrates the thermal behaviour of the electrolyte when using  $\text{CaCrO}_4$  as a depolarizer. It is seen that the first peak starts at  $69^\circ\text{C}$  and terminates at  $110^\circ\text{C}$ , which is an exothermic process that results from the elimination of water molecules linked to the sample, which is generally a weak physical linkage. After  $110^\circ\text{C}$  and up to  $185^\circ\text{C}$ , ascending for the curve is noticed. This is referred to the elimination of water molecules, which are chemically bonded to the sample. It is

believed that the depolarizer causes this ascending during the exothermic process, which decreases the covalency character for the sample components, *i.e.*, increases the ionic character. This led to the ascension of the temperature and the appearance of the molten LiCl, which is higher than that with the absence of the depolarizer. This means that the depolarizer changed the crystalline structure of LiCl and consequently alters the distance between  $\text{Li}^+$  and  $\text{Cl}^-$  to increase the m.p. After  $185^\circ\text{C}$ , strong descending for the curve is observed indicating the appearance of endothermic process and the melt of one of the salts which is thought to be LiCl. After  $219^\circ\text{C}$  till  $316^\circ\text{C}$ , stabilization of the curve takes place which indicates the melt of LiCl alone. At a temperature higher than  $316^\circ\text{C}$ , a sharp peak emerges indicating an exothermic process, where a eutectic salt is formed as a result of dissolving KCl into the molten LiCl, and the maximum of this case falls at  $347^\circ\text{C}$ . Then, around  $380^\circ\text{C}$ , the curve is stabilized, which is a stabilized situation for the eutectic mixture. The heat content for this process is  $88 \text{ J g}^{-1}$ , which is much greater than that for the eutectic state of the first sample, where no depolarizer was used. Here, we find an increase in the heat content for the melt process and consequently an increase in the produced voltage. This seems in accord with the results observed in the determination of the weight percentage for the depolarizer  $\text{CaCrO}_4$  with a mixture of salts. The study showed that the depolarizer  $\text{CaCrO}_4$  gave the highest voltage (0.8 V) for the operated cell. The anticipated reason is the ability of  $\text{CaCrO}_4$  to dissolve into this molten salt, which leads to a high electrolytic conductivity within the cell electrolyte preventing depolarization at the electrodes.

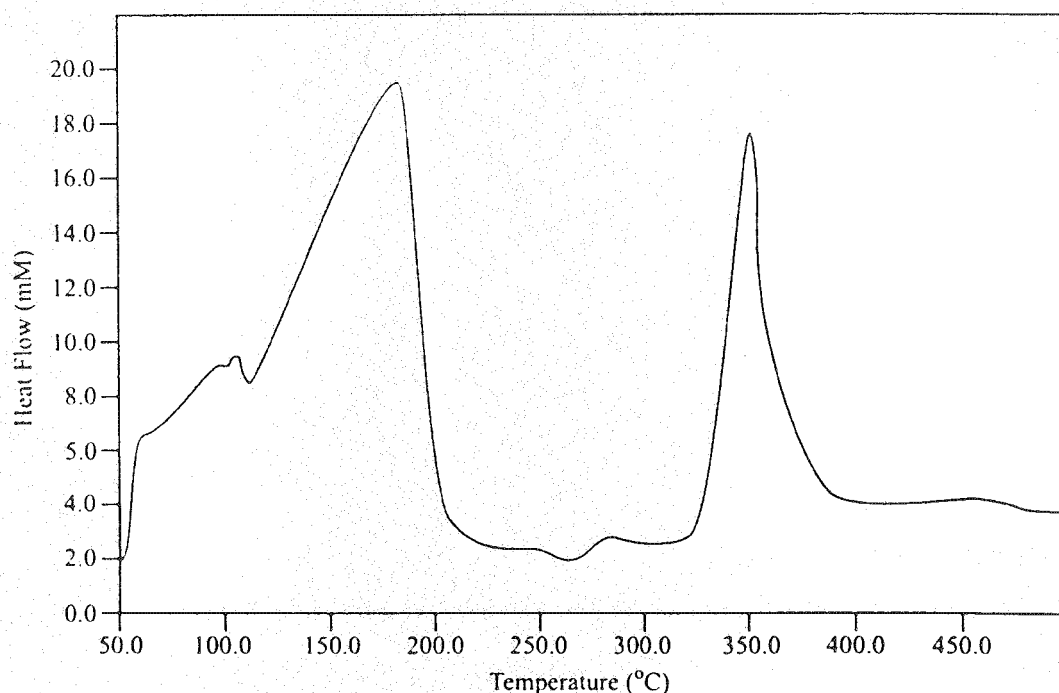


Fig. 4. The thermal behaviour of the electrolyte in the presence of  $\text{CaCrO}_4$

Fig. 5 shows the thermal behaviour of the electrolyte when the depolarizer,  $\text{K}_2\text{Cr}_2\text{O}_7$ , was used. It is recognized that the curve starts ascending at  $4^\circ\text{C}$ , which continues up to  $160^\circ\text{C}$ . This is an exothermic process arising from the elimination of the crystallization water. This comes as a result of the molten preparation process. After that, descending of the curve is noticed as a result of the depolarizer



effect upon LiCl, which starts melting at 240°C. It is believed that  $K_2Cr_2O_7$  affects KCl raising its m.p. and ascending the ionic character. This is referred to the ability of  $K_2Cr_2O_7$  to provide the molten salt with  $K^+$  which causes the precipitation of KCl and raising the m.p. Here, we find a new eutectic state between  $K_2Cr_2O_7$  and KCl at 299°C. Its thermal content is  $40 J g^{-1}$  which is half that obtained with the depolarizer  $CaCrO_4$ .

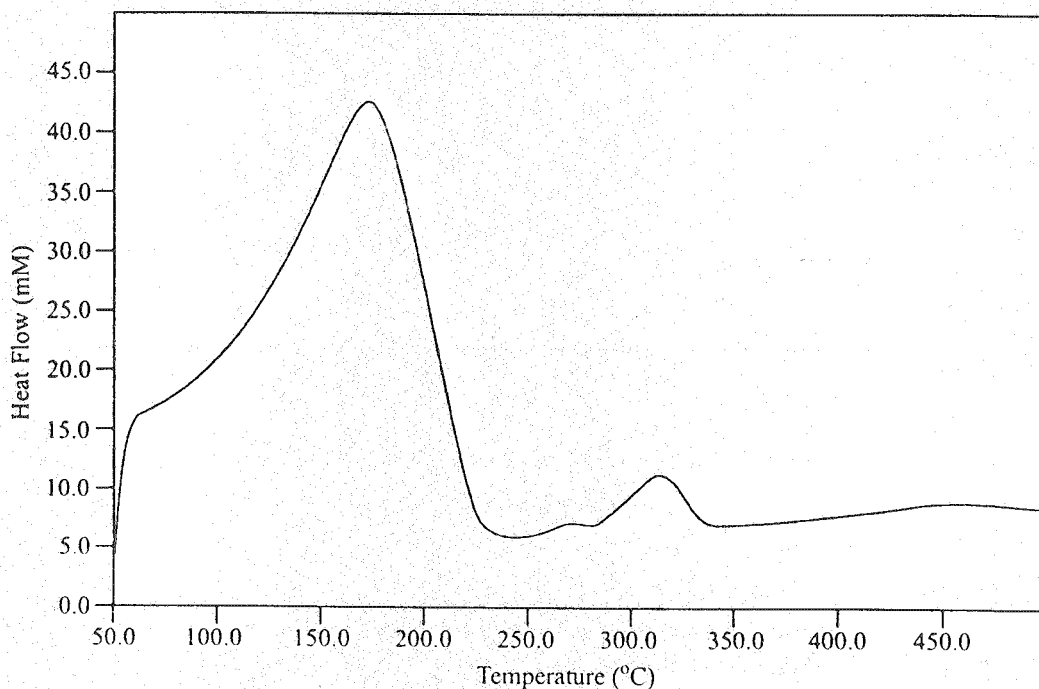


Fig. 5. The thermal behaviour of the electrolyte in the presence of  $K_2Cr_2O_7$

The thermal behaviour of the electrolyte in the presence of the depolarizer,  $K_2CrO_4$ , is shown in Fig. 6. Four peaks appear. The first one starts at 64°C, where the curve starts ascension as a result of an exothermic process resulting from losing the crystallization water formed from the salt preparation, which should be carried out at rigorous air-free atmosphere. The peak attained the top at 149°C; then, the curve declines, indicating the occurrence of endothermic process, which emerges from the effect of the depolarizer upon LiCl, where an expected increase in the covalency character takes place, leading to a decrease in the m.p. The curve continues to descend till 195°C to be stabilized up to 301°C, where a new anticipated eutectic state between  $K_2CrO_4$  and LiCl appears. The top of this change is at 322.8°C, then starts descending until 331.8°C to start ascending at 332°C, where a recrystallization process for  $K_2CrO_4$  arises.  $K_2CrO_4$  is then converted to  $K_2Cr_2O_7$  displaying a top at 344.5°C. After this, the eutectic state originates at 351°C, where eutectic mixture between LiCl and KCl takes place. The sharp peak observed at 359.5°C represents the eutectic state for the salts in the presence of  $K_2CrO_4$  as a depolarizer. The heat content for this process is  $20.8 J g^{-1}$ . It appears at higher temperature than that when the depolarizer,  $CaCrO_4$ , is used, and with lower thermal content. This denotes a decrease in the thermal content for this electrolyte as shown from decrease in the voltage in case of using the depolarizer,  $K_2CrO_4$ .

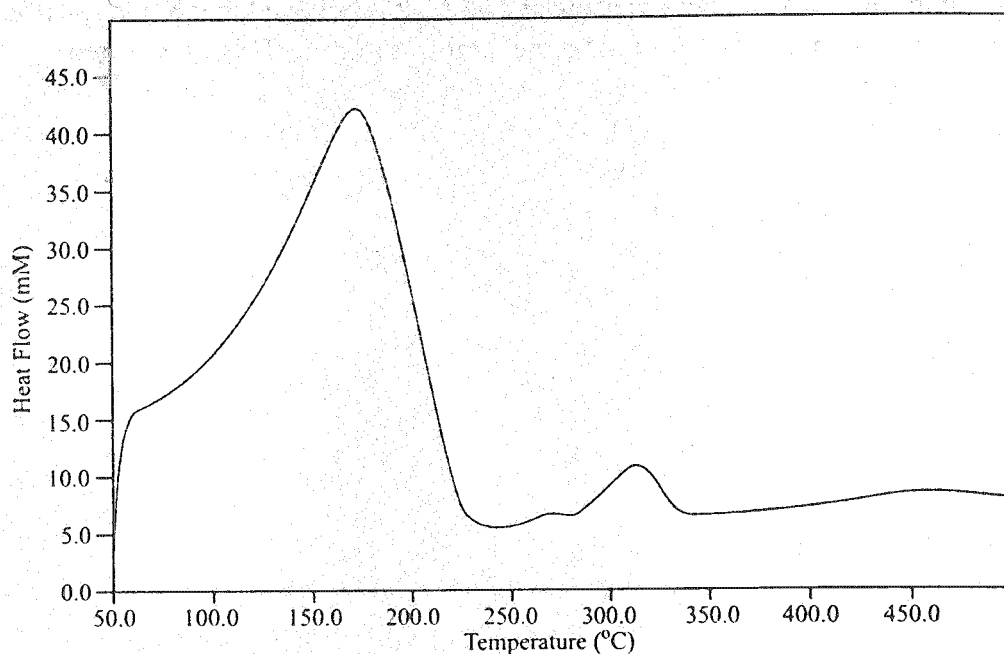


Fig. 6. The thermal behaviour of the electrolyte in the presence of  $K_2CrO_4$

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