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HEAT OF REACTION DETERMINATIONS IN THE SYSTEM Ca–LiCl–KCl–CaCrO$_4$–SiO$_2$ USING DIFFERENTIAL SCANNING CALORIMETRY*

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ABSTRACT

As a result of the observation of heat generation in electrochemical thermal cells of the type $^{-}$Ca|LiCl–KCl, SiO$_2$, CaCrO$_4$|Fe$^+$, heats of reaction of the Ca–LiCl–KCl–CaCrO$_4$–SiO$_2$ system were investigated using differential scanning calorimetry. Three significant reactions were studied, all involving calcium. Calcium reacts rapidly with LiCl immediately upon melting of the LiCl–KCl eutectic mixture at 352°C. The exothermic reaction expressed as

$$2\,Ca + 2\,LiCl \rightarrow CaCl_2 + CaLi_2$$

has a heat of reaction equal to -1.4 kcal (-17.5 cal/g Ca). Calcium undergoes a rapid and highly exothermic reaction with CaCrO$_4$ which occurs at the melting point of the LiCl–KCl–CaCrO$_4$ ternary eutectic mixture (342°C). Expressing this reaction as

$$3\,Ca + 2\,CaCrO_4 + 2\,LiCl \rightarrow 2\,Ca_2CrO_4Cl + CaLi_2$$

the heat determined was -212 kcal (-1770 cal/g Ca). Calcium reacts with SiO$_2$ at much higher temperatures (400–600°C) also in a strongly exothermic manner. The Ca/SiO$_2$ reaction is considerably slower than the other two reactions studied. For the reaction expressed as

$$4\,Ca + SiO_2 \rightarrow 2\,CaO + Ca_2Si$$

the heat of reaction is -106 kcal (-664 cal/g Ca).

INTRODUCTION

Thermal batteries are electrochemical batteries containing an electrolyte which is solid and virtually non-conductive at ambient temperatures; however, when heated above its melting point, the electrolyte becomes an excellent ionic conductor, thereby rendering the battery capable of supplying power at relatively high rates. The electrochemical cells used in thermal batteries frequently employ a calcium anode, a LiCl–

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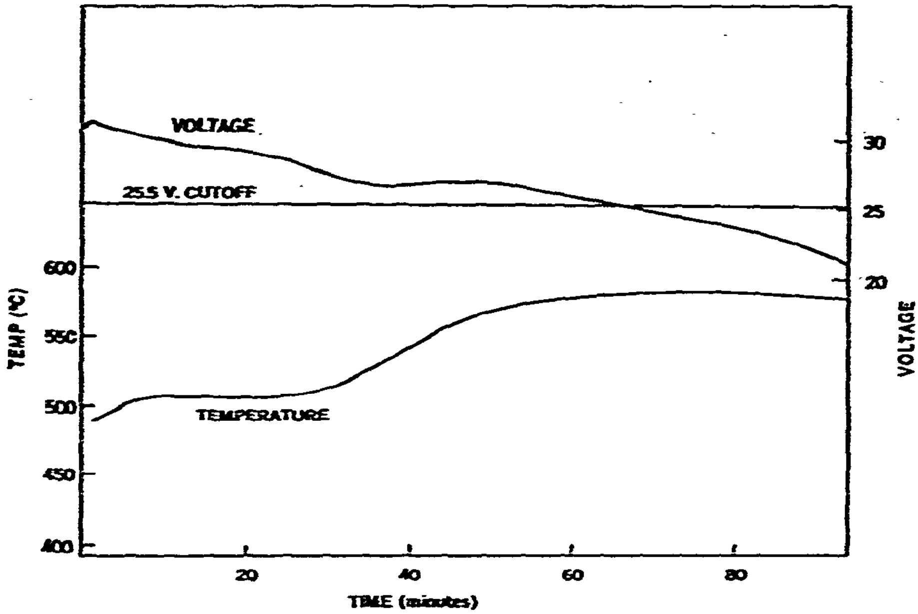

Fig. 1. Voltage and temperature vs. time for a thermal battery (thermally balanced).

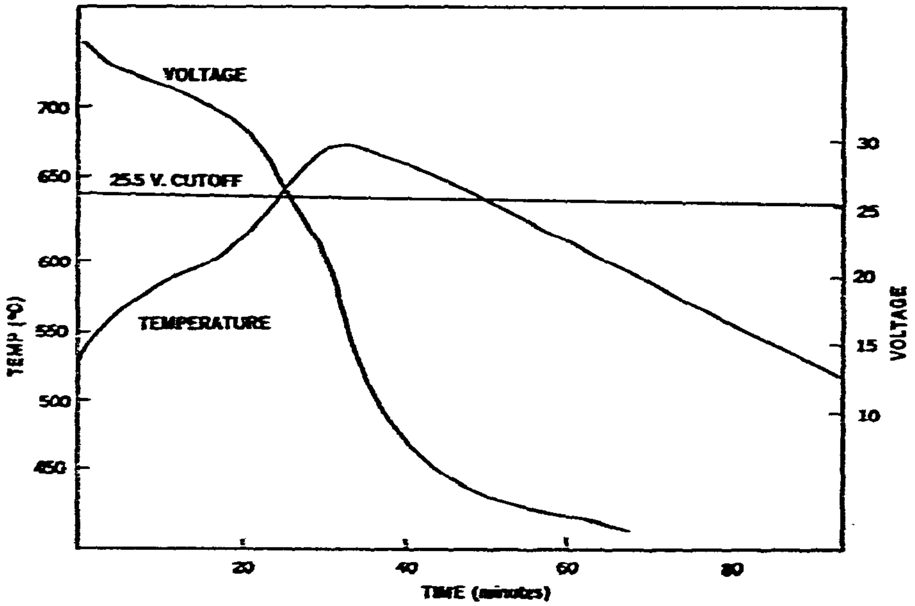

Fig. 2. Voltage and temperature vs. time for a thermal battery (overheated).

KCl eutectic mixture as the electrolyte, and a cathodic depolarizer of $CaCrO_4$. The LiCl, KCl, and $CaCrO_4$ are commonly mixed together with finely divided SiO_2 added as a binder and pressed into a tablet which is then placed adjacent to the Ca anode[1]. It has been demonstrated in our laboratory that, in an activated thermal cell of this type, heat-generating chemical reactions involving some or all of these materials occur during the cell discharge. This is illustrated in Fig. 1 which shows both battery

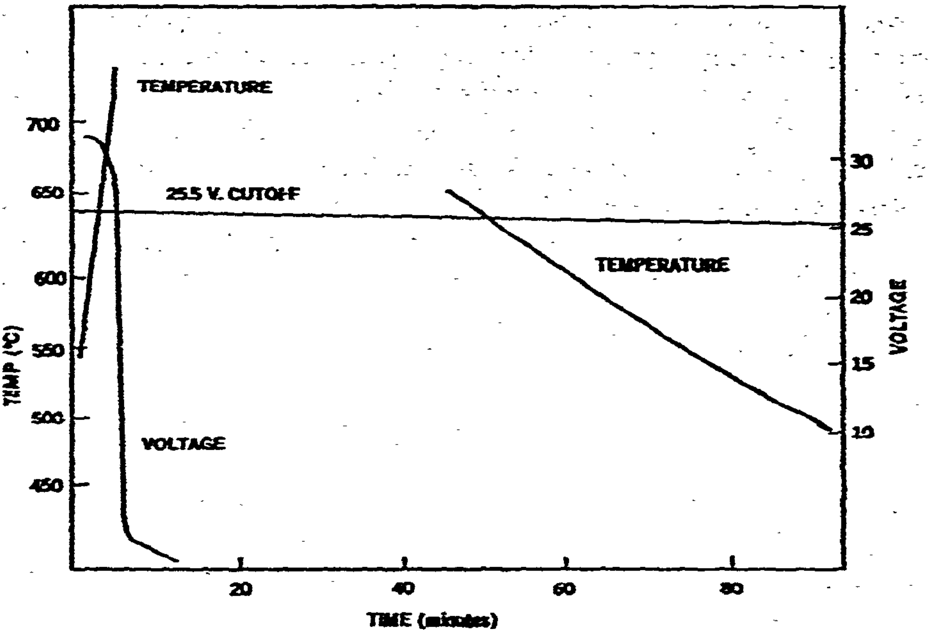

Fig. 3. Voltage and temperature vs. time for a thermal battery (thermal runaway).

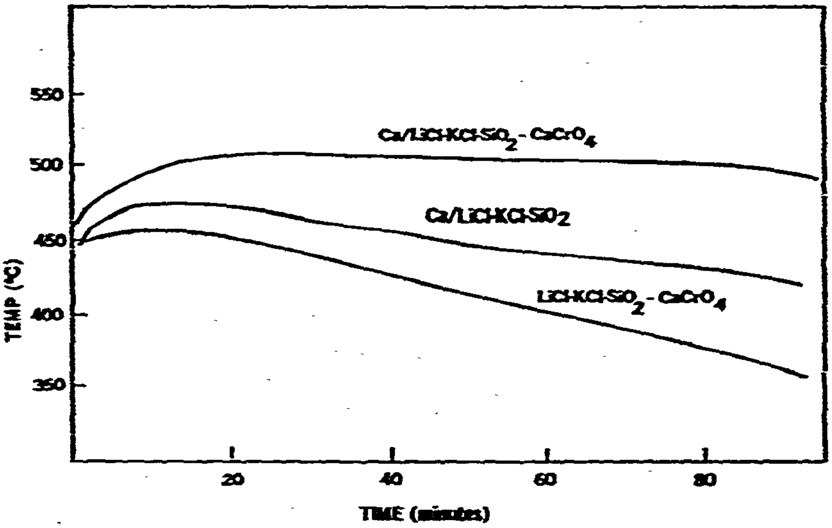

Fig. 4. Temperature vs. time for thermal batteries of various cell compositions.

voltage and cell temperature as a function of time for a long-life thermal battery. The temperature increase observed, beginning about 30 min after battery activation, is indicative of heat-generating chemical reactions. Observation of the voltage–time curve shows that active life of the thermal battery is prolonged by this heat generation. Figure 2 shows that excessive heat generation can result in a rapid voltage loss and shortened battery life. Figure 3 illustrates a catastrophic failure condition called "thermal runaway" which occurs in thermal batteries and results in rapid destruction of the battery's ability to deliver power.

In order to measure the effect of calcium and $CaCrO_4$ on the temperature–time curves, two experimental batteries were activated, one with no calcium anodes and the other with no $CaCrO_4$ present. Results for these two batteries are compared with a curve for a standard battery in Fig. 4. It may be noted that removing $CaCrO_4$ lowers the temperature profile and that removal of Ca decreases the temperature still further.

These data show that heat generation can be either beneficial or harmful and that Ca and $CaCrO_4$ are involved in the heat generating reactions. In order to better understand and control the processes responsible for heat generation in thermal batteries, an investigation of the reactions in the Ca–LiCl–KCl–$CaCrO_4$–SiO_2 system and the associated heats of reaction was undertaken.

EXPERIMENTAL

Materials used in this investigation included "high purity–low oxygen" calcium sheet 0.013 cm thick (99.3% Ca, 0.3% O) from Ventron Corporation, Beverly, MA; reagent grade LiCl and KCl, both vacuum dried for 16 h at 120°C; high-purity $CaCrO_4$ (assay 99.85%) prepared from reagent grade $CaCO_3$ and Na_2CrO_4 using a method previously described[2] and vacuum dried for 16 h at 120°C; and a high-purity (99%), small-particle size SiO_2 (Cab-O-Sil EH-5) from Cabot Corporation, Boston, MA, which was dried at 600°C for 4 h.

The calcium was degreased with trichloroethylene, punched in 0.32 cm diameter discs, cleaned with a solution of 5% HNO_3 in acetone, rinsed in acetone, and air dried. Samples of LiCl–KCl eutectic were prepared by fusing the appropriate amounts of the two individual salts (41.0 mole % LiCl) in a quartz tray at 650°C for 1 h, cooling to room temperature, and grinding to a powder. LiCl–KCl–$CaCrO_4$ samples were prepared in the ternary eutectic composition (57.3 mole % LiCl–39.8% KCl–2.8% $CaCrO_4$) by adding the required amount of $CaCrO_4$ to the LiCl–KCl eutectic sample, fusing at 450°C in a quartz tray, cooling and grinding. Samples with SiO_2 were prepared by adding 5 wt. % SiO_2 to either the LiCl–KCl or the LiCl–KCl–$CaCrO_4$ eutectics and ballmilling for 2 h to obtain a homogeneous mixture.

The Perkin-Elmer Model DSC-II was used for all thermal analyses. It was necessary to contend with numerous experimental problems in the DSC investigation, including reaction with the atmosphere, reaction with the sample pan, two or more competing reactions within the sample mixture itself, incomplete reactions, creeping of molten samples, and volatilization of reactants and/or products. The optimum experimental conditions included the use of a molybdenum sample pan (0.32 cm i.d.) which in turn was sealed under an argon atmosphere inside a standard Perkin-Elmer gold pan designed for use with volatile samples. Salt samples varied between 0.1 and 10.0 mg in weight, and the heating rates employed ranged from 0.5 to 20°C/min. DSC scans were from 150 to 700°C.

Since most samples contained the LiCl–KCl eutectic, that mixture was usually used for calibration of the DSC. Values for the melting point (352°C) and the heat of fusion (56.1 cal/g) of the LiCl–KCl eutectic have been previously established[3]. In some instances, the LiCl–KCl–$CaCrO_4$ eutectic (m.p. 342°C and heat of fusion 52.3 cal/g)[4] was used as a standard. When DSC samples contained both calcium and a salt, the powdered salt was placed between two calcium discs to assure complete reaction.

X-Ray diffraction analysis was used in the identification of reaction products. Materials used for X-ray analysis were not the DSC samples, but were larger samples reacted together in an argon-filled glove box. These larger samples were needed in order to obtain sufficient quantities of products for analysis.

RESULTS

DSC determinations were made for Ca alone, LiCl–KCl eutectic, $CaCrO_4$ alone, SiO_2 alone, Ca + LiCl–KCl, Ca + $CaCrO_4$, Ca + SiO_2, LiCl–KCl–$CaCrO_4$ eutectic, LiCl–KCl + SiO_2, LiCl–KCl–$CaCrO_4$ + SiO_2, Ca + LiCl–KCl–$CaCrO_4$, Ca + LiCl–KCl + SiO_2, and Ca + LiCl–KCl–$CaCrO_4$ + SiO_2. Three significant reactions were detected and all involved calcium: Ca + LiCl (in the LiCl–KCl eutectic); Ca + $CaCrO_4$ (in the LiCl–KCl–$CaCrO_4$ eutectic); and Ca + SiO_2 (when mixed with either the LiCl–KCl or the LiCl–KCl–$CaCrO_4$ eutectic).

Ca + LiCl. The types of curves obtained from this mixture are shown in Fig. 5. The net difference in area between the DSC curves for LiCl–KCl and for Ca + LiCl–KCl yields the heat for the Ca + LiCl reaction. This heat may either result in a reduced endothermic peak, as in the case for the curve at the left of Fig. 5, or it may show a small exothermic peak following the LiCl–KCl melting endotherm as in the curve on the right. Calcium is known to react with LiCl to form a calcium–lithium alloy[5]. The overall reaction may be written as

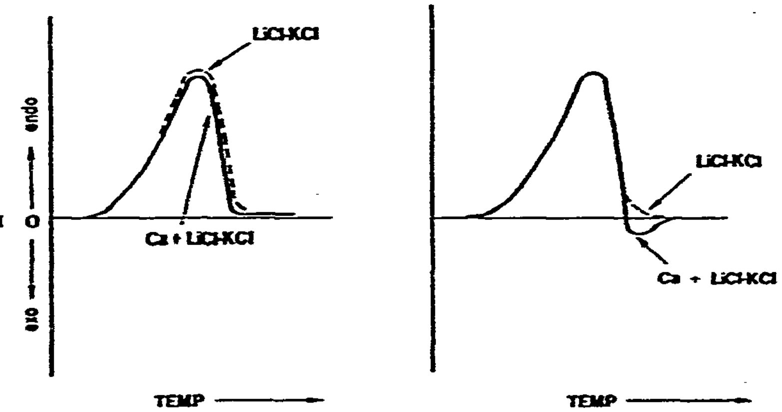

Fig. 5. DSC curves for Ca + LiCl–KCl eutectic.

$$2\,Ca + 2\,LiCl \rightarrow CaCl_2 + CaLi_2\ (alloy) \qquad (1)$$

This reaction may be considered the sum of two other reactions

$$Ca + 2\,LiCl \rightarrow CaCl_2 + 2\,Li \qquad (2)$$

$$Ca + 2\,Li \rightarrow CaLi_2\ (alloy) \qquad (3)$$

The reaction occurs at the melting point of the LiCl–KCl eutectic (352 °C). At that temperature the Ca–Li alloy is molten, as shown by the Ca–Li phase diagram[6]. This molten active-metal alloy will react with most sample pan materials, thus necessitating the use of molybdenum which is inert to both the molten alloy and the molten salts.

The heat of reaction for reaction (1) is −1.4 kcal or −17.5 cal/g Ca. The existence of $CaCl_2$ as a product was shown by X-ray diffraction. $CaLi_2$ alloy was detected by cooling the reaction mixture and observing the alloy freezing point at 230 °C. The standard error on this determination was quite large because the technique involves measuring a small difference between two large numbers. The standard error of the mean was ± 0.2 kcal (~ 14%).

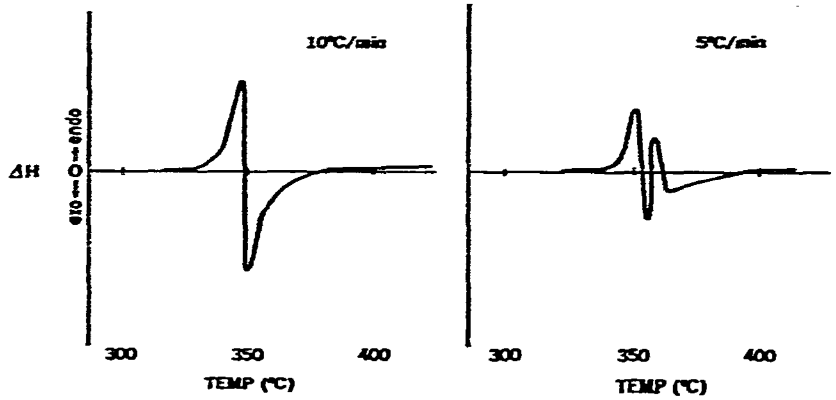

Fig. 6. DSC curves for Ca + $CaCrO_4$(LiCl–KCl).

Ca + $CaCrO_4$. Calcium and calcium chromate react in a very rapid, highly exothermic manner upon melting of the LiCl–KCl–$CaCrO_4$ ternary eutectic. Examples of the resulting DSC curves are shown for two different heating rates in Fig. 6. These curves can be explained in the following manner. At 10 °C/min the curve shows an initial melting endotherm followed by a net exotherm as the Ca/$CaCrO_4$ reaction takes place. The melting is completed by the time the exothermic chemical reaction subsides. At the slower heating rate (5 °C/min) the curve again shows an initial endotherm which is replaced by an exotherm as the Ca/$CaCrO_4$ reaction proceeds. When the chemical reaction begins to slow, the salt has not yet become completely molten and consequently the curve swings back to a net endotherm. Following completion of the melting, the curve again goes exothermic as the Ca/$CaCrO_4$ reaction goes to completion. Total heat is measured from the DSC curve and corrections are made for the LiCl–KCl–$CaCrO_4$ eutectic melting endotherm and for the exothermic Ca + LiCl reaction.

It is not certain whether $CaCrO_4$ reacts with the calcium per se or with the Ca–Li alloy formed via the Ca + LiCl reaction. X-Ray diffraction studies have identified one of the reaction products as a Cr(V) compound, Ca_2CrO_4Cl. DSC

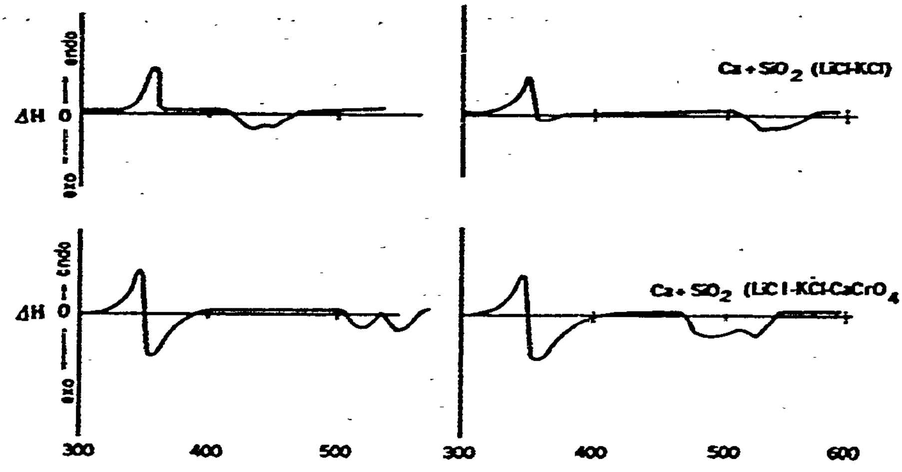

Fig. 7. DSC curves for Ca + SiO_2(LiCl–KCl) and for Ca + SiO_2(LiCl–KCl–$CaCrO_4$).

cooling curves have shown the existence of the Ca–Li alloy in the mixture following completion of the reaction. This suggests the reaction scheme

$$3\ Ca + 2\ CaCrO_4 + 2\ LiCl \rightarrow 2\ Ca_2CrO_4Cl + CaLi_2 \qquad (4)$$

The measured heat for this reaction is −212 kcal or −1770 cal/g Ca. The precision of the determinations of this value was considerably better than for the Ca + LiCl reaction. The standard error of the mean was ± 7 kcal or ~ 3%.

Ca + SiO_2. The reaction between calcium and silica is also highly exothermic, but the reaction occurs much more slowly than do the other two reactions. This may be because the SiO_2 is an insoluble solid as opposed to the previous cases where both LiCl and $CaCrO_4$ were in the liquid phase. The reaction between Ca and SiO_2 takes place between 400 and 600°C, well above the melting temperatures of either the LiCl–KCl (352°C) or the LiCl–KCl–$CaCrO_4$ (342°C). The DSC curves are shown in Fig. 7 and exhibit a more drawn-out exotherm than was observed for the other reactions. These curves were obtained at the same heating rate (10°C/min) and illustrate the variability in shape and temperature range observed for the Ca/SiO_2 reaction.

The heat for the reaction expressed as

$$4\ Ca + SiO_2 \rightarrow 2\ CaO + Ca_2Si \qquad (5)$$

is −106 kcal or −664 cal/g Ca. X-Ray diffraction analysis has shown CaO and Ca_2Si to be the reaction products. Since the reaction occurs well after the melting of the electrolyte and also after the occurrence of the Ca + LiCl and Ca + $CaCrO_4$ reactions, the heat resulting from the Ca + SiO_2 reaction can be read directly from the DSC curve with no corrections for other thermal events. There was some uncertainty in the exact concentration of the SiO_2 in the reaction mixture. This is a result of difficulties in obtaining very small samples which were representative of the overall composition. Consequently, over 150 samples were run with a standard error of the mean equal to ± 6 kcal (~ 6%).

The results of the determinations are summarized in Table 1.

TABLE 1

SUMMARY OF REACTIONS IN THE SYSTEM $Ca–LiCl–KCl–CaCrO_4–SiO_2$

Reaction	*Temperature (°C)*	*Heat of reaction (kcal)*
$2\,Ca + 2\,LiCl \rightarrow CaCl_2 + CaLi_2$	352	-1.4 ± 0.2
$3\,Ca + 2\,CaCrO_4 + 2\,LiCl \rightarrow 2\,Ca_2CrO_4Cl + CaLi_2$	342	-212 ± 7
$4\,Ca + SiO_2 \rightarrow 2\,CaO + Ca_2Si$	400–600	-106 ± 6

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