Asian Journal of Chemistry Vol. 19, No. 1 (2007), 758–764

X-ray Absorption Studies of the Catholyte Layer Components in Thermal Batteries

FALAH H. HUSSEIN*, AHMED N. ALKHATEEB†, KAREEM D. OMRAN and WALEED M. SARHAN‡

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

E-mail: abohasan_hilla@yahoo.com

Investigation of the X-ray diffraction values, for the catholyte components of the foreign cell and the linear spectrum for the diffraction values of these components, has been performed. Six obvious peaks appertaining to KCl, $CaCrO_4$ and LiCl have been recorded demonstrating that these compounds are the main components of the DEB layer. No peak for the binder has been identified due to its very low concentration, which did not exceed 5%. In addition, a similar study was accomplished for the assembled cell, before running the thermal cell, *via* the definition of the peaks appertaining to the catholyte components and the amplitudes d-values. The peaks for the compounds used in the preparation of the catholyte layer, that is, KCl, $CaCrO_4$ and LiCl have appeared. However, no peak was observed for the binder due to its low concentration. Furthermore, a comparison for the X-ray diffraction values and the linear spectrum for this diffraction for the catholyte layer of the assembled thermal cell, at different temperatures, namely, 400, 460 and 600°C; has been carried out. At 400°C the findings revealed that this layer contained the compounds KCl, $CaCrO_4$ and the alloy, $CaLi_2$. Nonetheless, at 460°C, the results demonstrated that the layer consisted of the compounds KCl, $CaCrO_4$, $CaCl_2$ and the oxides mixture, $Cr_2O_3{\cdot}2CaO$. However, the bands pertaining to $CaLi_2$ and LiCl obtained at 400°C have disappeared indicating the reaction between Ca and Li ions to form the mentioned alloy, followed by the breakdown of this alloy with the release of electrons. Finally, at 600°C, the results confirm the existence of $CaCrO_4$ and KCl besides the disappearance of the peaks belonging to $CaCl_2$. In addition, a peak has emerged for LiO_2, which was produced from the electrochemical reaction.

Key Words: Thermal batteries, Thermal cells, X-ray, Catholyte layer.

INTRODUCTION

A thermal battery consists of serial-connected thermal cells[1]. Configuration of the battery cell is composed of an anode, catholyte layer and the pyrotechnic heat source, which connects the cells. Concerning the catholyte layer, it is composed of three components, namely, the depolarizer (D), the electrolyte (E) and the binder (B). Regarding the depolarizer, usage of many materials such as K_2CrO_4, $CaCrO_4$, $CuCrO_4$, Fe_2O_3, $PbCrO_4$, V_2O_5 and WO_3 have been reported[2]. The electrolyte is a molten salt which has the prominent characteristics comprising the excellent conductivity, stability at 250°C above the melting point and good

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

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

solving ability for the products formed at the electrodes, throughout the thermochemical reaction.The standard electrolyte that has been employed over the years is the LiCl-KCl eutectic which melts at 352°C. However, LiCl-LiBr-LiF eutectic, which melts at 436°C, has proved to have the best rate and power characteristics. It shows very low polarization due to the absence of Li(+) gradients, common with the LiCl-KCl mixture[4]. Pertaining to the binder (B), the widely applied one is SiO_2.

In our previous study[1], the catholyte layer, included within an efficient thermal cell, was assembled by blending the three components, $CaCrO_4$, K_2CrO_4 or K_2CrO_7, as the depolarizer (D), LiCl-KCl eutectic mixture as the electrolyte (E) and SiC_2 as the binder (B). Investigation the catholyte layer effect, where the anode was Ca, showed that that the weight percentage 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), $CaCrO_4$ and the binder, SiO_2 of 83 and 17% respectively, generated the maximum produced voltage of 0.8 V at 460–465°C.

The present project aimed to accomplish a comparative X-ray investigation for the catholyte layer of the foreign thermal cell and that of the assembled one, before and after running the thermal cell, by measuring the diffraction values and plotting the linear spectra for the components and comparing the results with those issued by the American Society for Testing Materials (ASTM). In addition, another comparison study of d-values at 400, 460 and 600°C has been intended to be carried out.

EXPERIMENTAL

All the used chemicals were purchased from BDH, E. Merck or Fluka, with purity 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 chemical compounds, resulting from electrochemical reactions of the catholyte layer in the thermal cell have been identified *via* the use of X-ray diffraction instrument. The procedure was described before[5].

Measurements were performed by using X-ray diffractometer (PW 1840, Philips). From the X-ray spectrum scheme, the amplitude d-values for the catholyte layer components were calculated by using the Bragg's equation. Since no crystalline forms with identical amplitude d-values can exist, a distinction between crystalline materials in a sample is possible by calculating the amplitude d-values for them, without the need to separate these materials from each other. The amplitude d-value was compared with that given by ASTM data[6].

RESULTS AND DISCUSSION

Table-1 and Fig. 1 display the X-ray diffraction values for the catholyte layer components of the disassembled foreign cell and the linear spectrum for the diffraction values of these components. The linear spectrum shows six obvious peaks appertaining to KCl, $CaCrO_4$ and LiCl. Therefore, it can be concluded that these compounds are the main components of DEB layer. Moreover, this ascertains the wide usage range for these three components in the manufacturing of the thermal cells catholyte layer. No peak for the binder was identified due to its very low concentration, which did not exceed 5%.

TABLE-1
A COMPARISON OF THE X-RAY DIFFRACTION FOR THE CATHOLYTE LAYER OF THE FOREIGN THERMAL CELL

d-Value for the diffraction of the component (Å)	The products	d-Value for the diffraction of the standard compound (Å)
3.160		3.146
2.233	KCl	2.224
1.820		1.816
3.645		3.620
1.845	$CaCrO_4$	1.851
2.698		2.680
2.899	LiCl	2.967

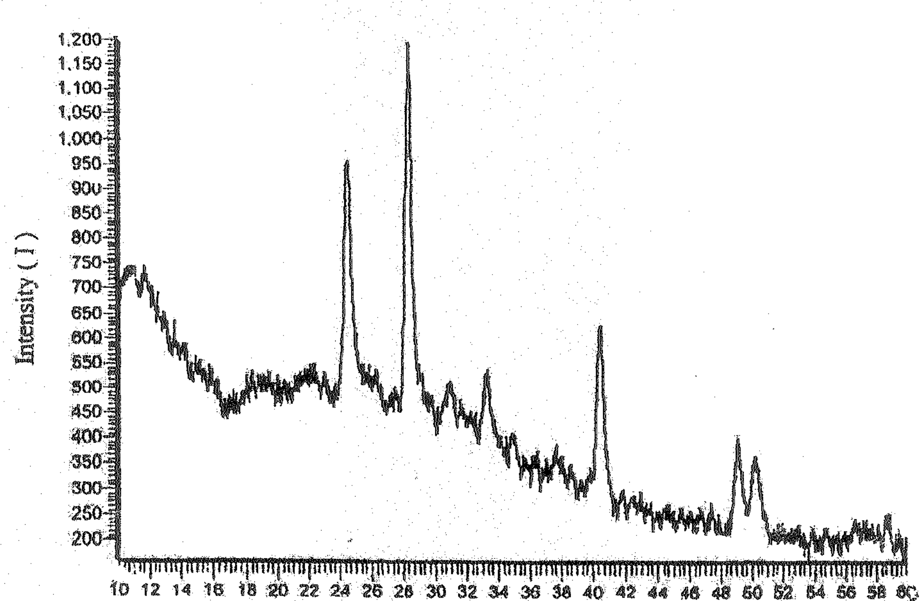

Fig. 1. The linear spectrum of the X-ray diffraction for the catholyte layer of the foreign thermal cell

Table-2 and Fig. 2 disclose the X-ray diffraction values for the catholyte layer of the assembled cell, before running, *via* the definition of the peaks appertaining to the catholyte components and the amplitude d-values and comparing what took place at different temperatures to be aware of the electrochemical products. The peaks for the compounds used in the preparation of the catholyte layer, that is, KCl, $CaCrO_4$ and LiCl have appeared throughout the linear spectrum for the deviation depicted in Fig. 4. However, no peak was observed for the binder due to its low concentration.

TABLE-2
A COMPARISON OF THE X-RAY DIFFRACTION FOR THE CATHOLYTE LAYER OF THE ASSEMBLED THERMAL CELL BEFORE THE OPERATION

d-Value for the diffraction of the component (Å)	The products	d-Value for the diffraction of the standard compound (Å)
3.160	KCl	3.150
2.229		2.224
1.816		1.816
1.567		1.573
3.015	LiCl	2.970
1.816		1.817
3.640	$CaCrO_4$	3.620
2.682		2.680
1.845		1.850
2.386		2.375
1.651		1.620

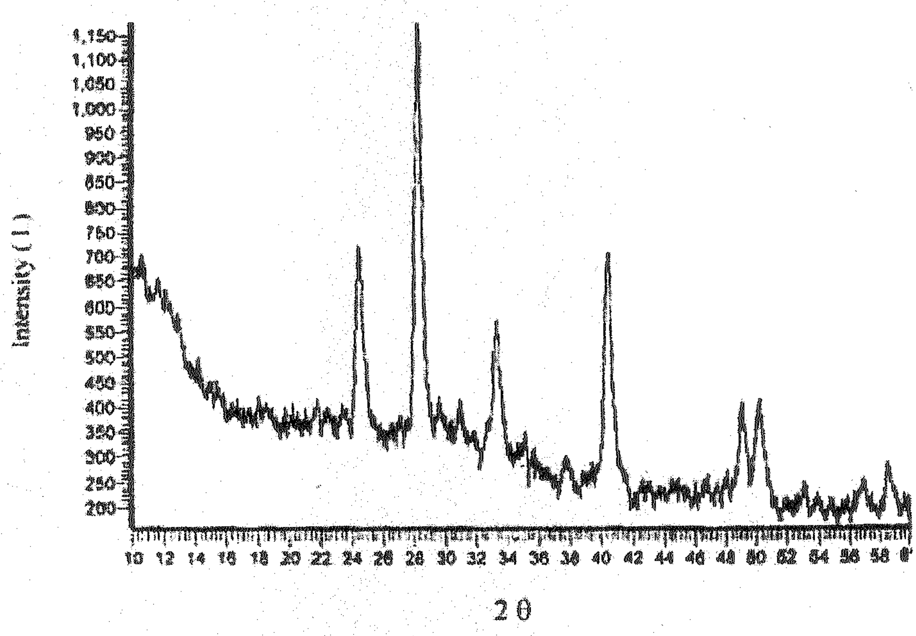

Fig. 2. The linear spectrum of the X-ray diffraction for the catholyte layer of the assembled cell before the operation

Table-3 and Figs. 3–5 reveal a comparison for the X-ray diffraction values and the linear spectrum for this diffraction, respectively, for the catholyte layer of the assembled thermal cell, at 400°, 460° and 600°C. Table-3 and Fig. 3 reveal that after running the cell at 400°C, the layer contained the compounds KCl, $CaCrO_4$ and the alloy, $CaLi_2$.

TABLE-3
A COMPARISON OF THE X-RAY DIFFRACTION FOR THE CATHOLYTE LAYER OF THE ASSEMBLED THERMAL CELL AT 400, 460 AND 600°C

Temperature (°C)	d-Value for the diffraction of the component (Å)	The products	d-Value for the diffraction of the standard compound (Å)
400	3.120 1.842 2.210	KCl	3.150 1.816 2.220
	3.590	$CaCrO_4$	3.620
	2.850 2.650 2.062	$CaLi_2$	2.890 2.680 2.041
460	3.17 2.23 1.819 1.573	KCl	3.150 2.220 1.820 1.575
	3.080 1.904 2.850	$CaCl_2$	3.050 1.906 2.858
	5.520 2.300	$Ca(CrO_2)_2$	5.510 2.290
	3.660 2.690 1.850	$CaCrO_4$	3.620 2.680 1.851
600	3.599 1.814	$CaCrO_4$	3.620 1.850
	3.120 2.209	KCl	3.140 2.220
	2.667	LiO_2	2.664

Table-3 and Fig. 4 demonstrate a comparison between the X-ray diffraction values of the catholyte layer of the assembled thermal cell and the linear spectrum of this diffraction at 460°C, respectively. This operation temperature has proved to be the most appropriate one, where a regular discharge took place beside the generation of the most stable voltage[7]. It is obvious that the layer comprehended the compounds KCl, $CaCrO_4$ as well as three peaks for $CaCl_2$. In addition, it contains the oxides mixture, $Cr_2O_3 \cdot 2CaO$. Nevertheless, the bands pertaining to

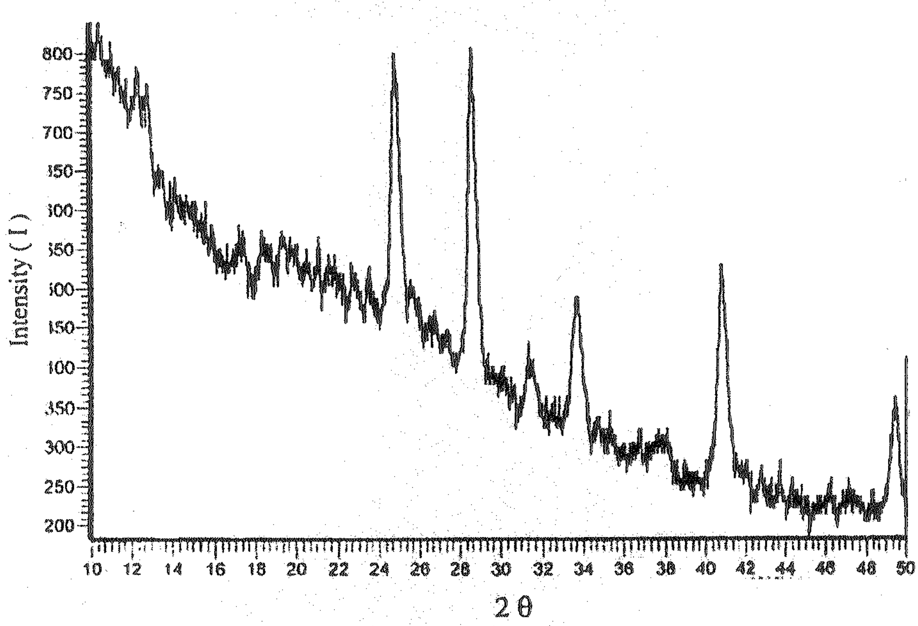

Fig. 3. The linear spectrum of the X-ray diffraction for the catholyte layer of the assembled thermal cell at 400°C

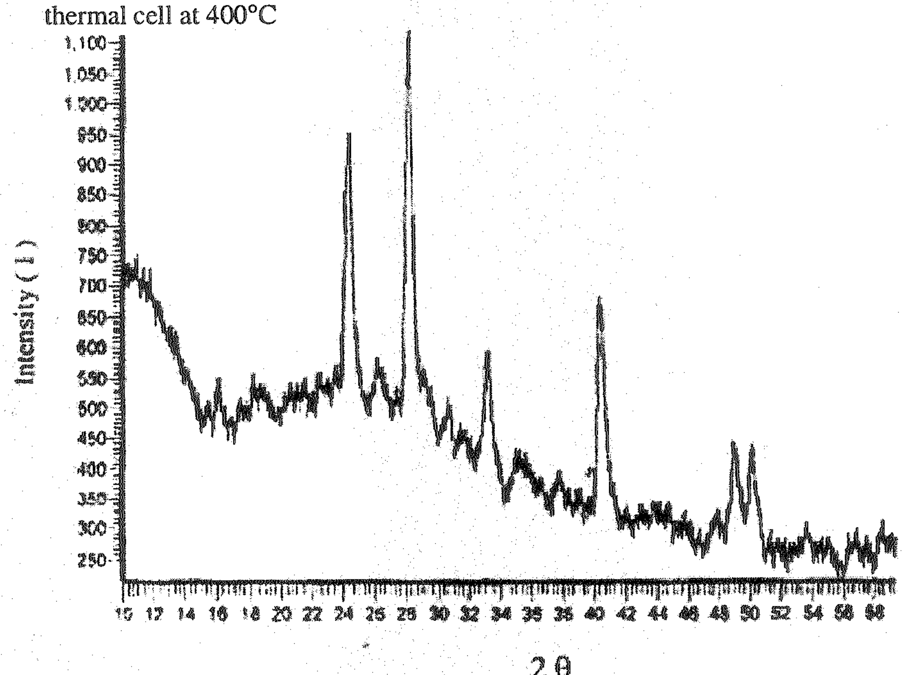

Fig. 4. The linear spectrum of the X-ray diffraction for catholyte layer of the assembled thermal cell at 460°C

$CaLi_2$ and LiCl, which exist at 400°C, have disappeared pointing out the taking place of the reaction between Ca and Li ions to form the mentioned alloy, followed by the breakdown of this alloy with the release of electrons. The suggested reaction is:

$$Ca^{2+} + 2Li^{+} \rightarrow CaLi_2 \quad (1)$$

$$CaLi_2 \rightarrow Ca^{2+} + 2Li^{+} + 2e^{-}$$

Table-3 and Fig. 5 represent a comparison for the X-ray diffraction and the linear spectrum for this diffraction, respectively, for the catholyte layer of the

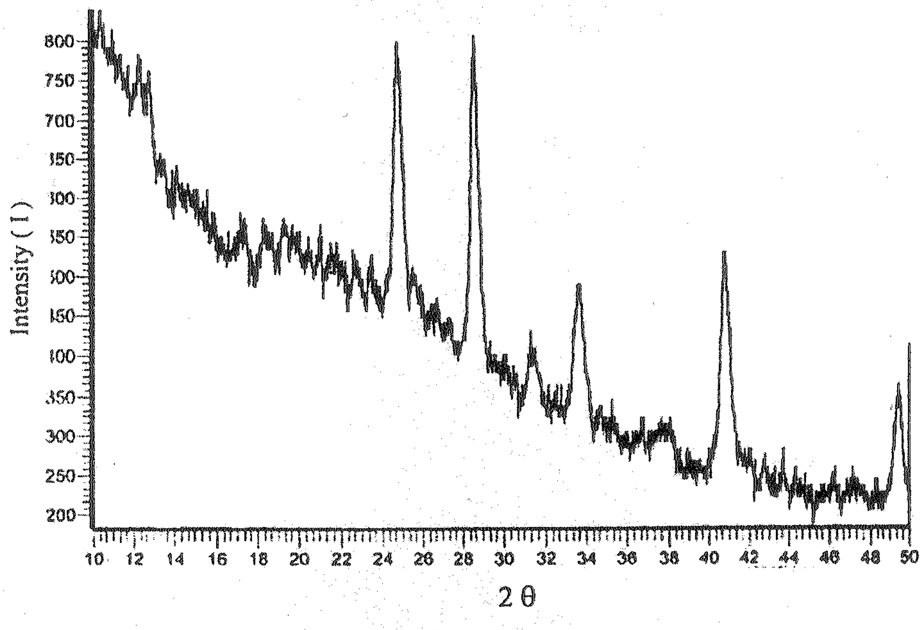

Fig. 5. The linear spectrum for the catholyte layer of the assembled thermal cell at 600°C

assembled thermal cell at 600°C. The existence of $CaCrO_4$ and KCl besides the disappearance of the peaks belonging to $CaCl_2$ is clearly observed. In addition, a peak has emerged for LiO_2 which was produced from the electrochemical reaction.

Tables 1–3 display that the d-values for the diffraction of the products, obtained from the thermochemical reactions, at the catholyte layer, are in excellent agreement with that published by ASTM for the standard analogues[6].

REFERENCES

1. W.M. Sarhan, A.N. Alkhateeb and F.H. Hussein, *Asian J. Chem.*, **18**, 397 (2006).
2. H.A. Laitinen and D.R. Rhodes, *J. Electrochem. Soc.*, **109**, 413 (1962).
3. H.A. Laitinen, R.P. Tisher and D.K. Roe, *J. Electrochem. Soc.*, **107**, 555 (1960).
4. R.A. Guidotti and F.W. Reinhardt, Electrolyte effects in Li(Si)/FeS_2 thermal batteries, Presented at the 19th International Power Sources Symposium, Brighton, England (1995).
5. F.H. Hussein, A.N. Alkhateeb, K.D. Omran and W.M. Sarhan, *Asian J. Chem.* (2006).
6. R. Jenkins and S.L Devries, An Introduction to X-ray Powder Diffractometry, N.V. Philips, Holland (1966).
7. W.M. Sarhan, A.N. Alkhateeb, K.D. Omran and F.H. Hussein, *Asian J. Chem.*, **18**, 982 (2006).

(*Received*: 7 March 2006; *Accepted*: 30 June 2006) AJC-5004