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A Comparative X-ray Investigation for the Anode Component in Thermal Batteries

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In this investigation, a comparative X-ray study for the anode of the foreign thermal cell and that of the assembled one have been carried out. The results have been compared with those issued by the American Society for Testing Materials (ASTM). A comparative investigation for the X-ray diffraction of the anode component of the foreign cell as well as the linear spectrum for the diffraction of this component revealed that this anode is a Ca electrode. The evidence came from the formation of $Ca(OH)_2$ accompanied by the liberation of H_2, as a result of the action of moisture on Ca. Six peaks of different intensities for $Ca(OH)_2$ were observed. A comparison for the X-ray diffraction values and the linear spectrum at 400°C, for the anode component of the assembled cell, has been carried out. After running the cell, the findings displayed that the electrode contained the compounds KCl, CaO, Li_2CrO_4, $CaCrO_4$, $Ca(OH)_2$ and $CaCl_2$, explaining the increment of the operation time for the cell, with a low voltage. The incomplete solubility of $CaCrO_4$ at 400°C gave rise to the slowdown of the thermochemical reactions, leading ultimately to the ascent of the operation period. A similar comparison was accomplished at 460°C; which is the temperature at which the cell was operating with maximum efficiency, to confirm that the anode mixture included $Ca(OH)_2$, CaO and $LiCrO_2$. Finally, a comparative study of the X-ray diffraction for the anode of the assembled thermal cell at 600°C, that was the temperature at which the complete consumption of the cell took place, disclosed throughout the amplitude d-values, that this electrode contained CaO, $Ca(OH)_2$ and the oxide mixture $LiO_2{\cdot}Cr_2O_3$. No change occurred upon the development of the compounds on the anode.

Key Words: Thermal batteries, Thermal cells, X-ray, Anode.

INTRODUCTION

Thermal batteries are primary batteries which have achieved their great importance as ideal power sources for military munitions from artillery shells all the way up to nuclear weapons. They are particularly useful for supplying

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short-term power in expendable weapons; such as missiles, mines and rockets and exploratory spacecraft like "Spirit" and "Opportunity" rovers, where thermal batteries were activated to facilitate carrying out the deployment which led to the safe arrival of Pathfinder Landers on the surface of Mars[4]. The importance of these batteries is attributed to their enormous features. They have long field storage life which exceeds 25 years, require no maintenance and operate over a wide range of temperatures, 350–600°C. In addition, they are highly reliable energy sources which are instantly activated to provide full power in several seconds and nominally produce 20 WHr/Ib[5].

In our previous study[6], an efficient high temperature molten salt thermal cell had been constructed. It was composed of Ca or Mg as the anode. 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 (B). In addition, the weight percentages of the depolarizer (D), $CaCrO_4$ and the binder (B), SiO_2 of 83% and 17%, respectively, generated the maximum produced voltage of 0.8 V at 460–465°C. As regards the anode, the findings revealed that with the Ca anode, a cathode composed of 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. In addition, mixtures of 75% $K_2Cr_2O_7$ and 25% SiO_2 and 30% K_2CrO_4 and 70% SiO_2 provided voltages of 0.41 and 0.48 volts. However, using Mg anode with the same mentioned eutectic mixture, a mixture of 90% $CaCrO_4$ and 10% SiO_2; and 78% $K_2Cr_2O_7$ and 22% SiO_2 afforded voltages of 0.42 V and 0.44 V respectively, demonstrating that Ca is more efficient than Mg.

The present paper aimed to accomplish a comparative X-ray investigation for the anode 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).

EXPERIMENTAL

All the used 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 chemical compounds, resulting from the electrochemical reactions of the anode in the thermal cell, have been identified *via* the use of an X-ray diffraction instrument, where a laboratory thermal cell was operated under specific conditions. Higher and lower temperatures than that for the thermal cell were utilized. In each run, the linear spectrum was recorded to identify the products.

The instrument recorded the X-ray spectrum plot, which represented the X-ray diffraction as abscissa in definite positions, 120 min, against the intensity (I/I_0) or the height of the peaks, as ordinate, depending upon using Bragg's equation.

This equation was used to convert the diffraction values from the angles (2θ) to surface distances (amplitude d-values):

$$n\lambda = 2d \sin \theta = d \sin \theta \tag{1}$$

Measurements were done by using X-ray diffractometer (PW 1840, Philips). From the X-ray spectrum scheme, the amplitude d-values for the components of the anode were calculated by using the above mentioned Bragg's equation. Since, no crystalline forms with identical amplitude d-values can exist, 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-values was compared with that given by ASTM data[7].

RESULTS AND DISCUSSION

Table-1 and Fig. 1 show a comparison between the X-ray diffraction for the anode component of the disassembled foreign cell and the linear spectrum for the diffraction of this component, respectively. It is clearly seen that this anode is a Ca electrode. The evidence came from the formation of $Ca(OH)_2$ accompanied by the liberation of H_2, as a result of the action of moisture on Ca, as follows:

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2 \tag{2}$$

Six peaks of different intensities for $Ca(OH)_2$ are observed. The result is compatible with what has been previously mentioned about the wide usage of Ca as an anode in the thermal cells[8].

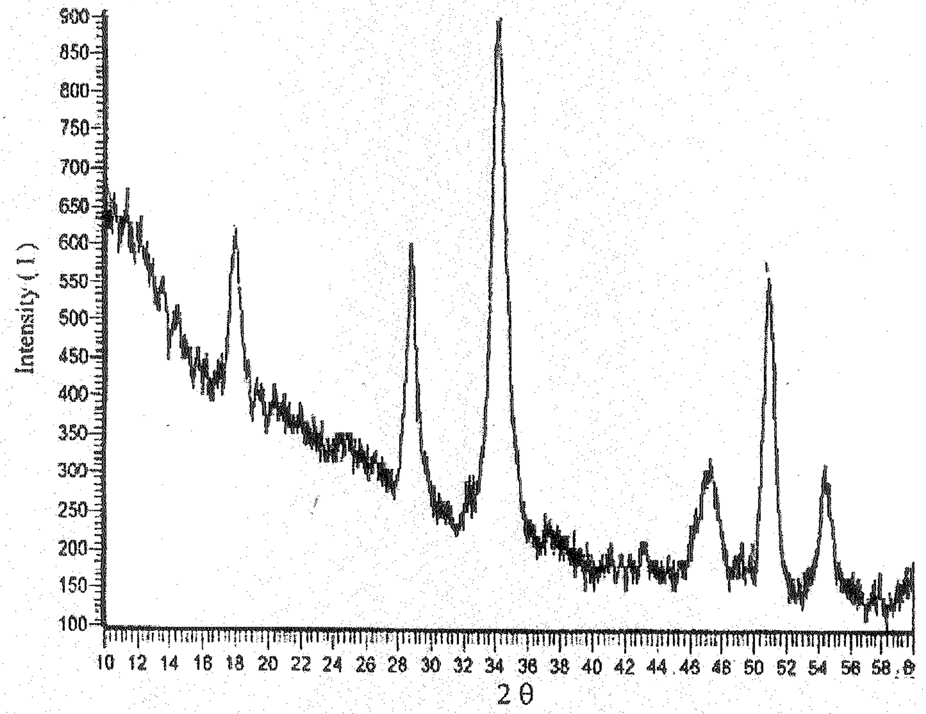

Fig. 1. The linear spectrum for the X-ray diffraction for the anode of the foreign thermal cell

Table-2 and Figs. 2–4 reveal a comparison for the X-ray diffraction values and the linear spectrum at 400°, 460° and 600°C for the anode component of the assembled cell, respectively. Table-2 and Fig. 2 reveal that after running the cell at 400°C, the electrode contains the compounds KCl, CaO, Li_2CrO_2, $CaCrO_4$, $Ca(OH)_2$ and $CaCl_2$. The formation of these compounds at this temperature explains the increment of the operation time for the cell, with a low voltage. The oxidant, $CaCrO_4$, which oxidized Ca in the presence of Li^+ to CaO and $LiCrO_2$, respectively was not completely soluble at 400°C and consequently decreased the rates of the thermochemical reactions leading to the increment of the operation time of the cell[9]. The suggested reaction is:

$$2Ca + 2Li^+ + 2CaCrO_4 \rightarrow 4CaO + 2LiCrO_2 + 2e^- \qquad (3)$$

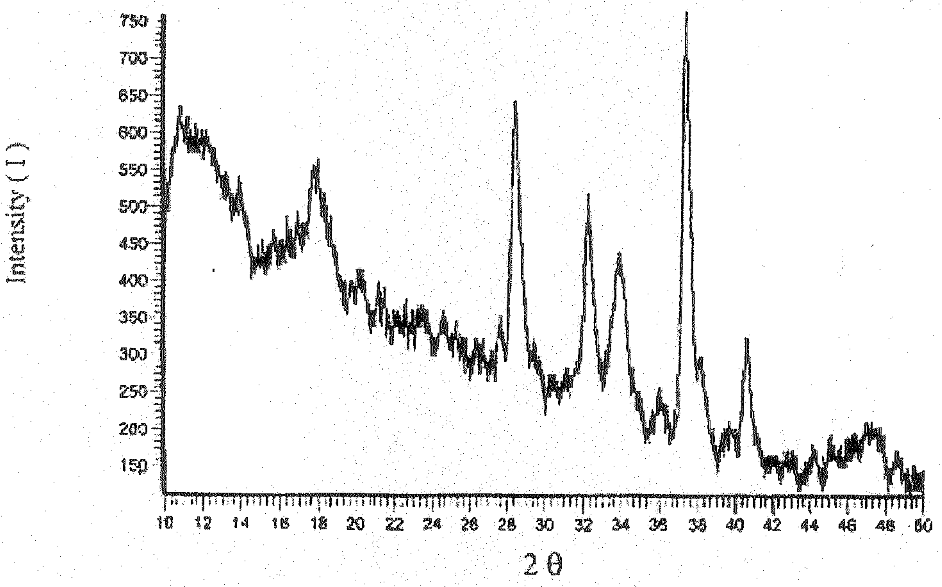

Fig. 2. The linear spectrum of the X-ray diffraction for the anode of the assembled thermal cell at 400°C

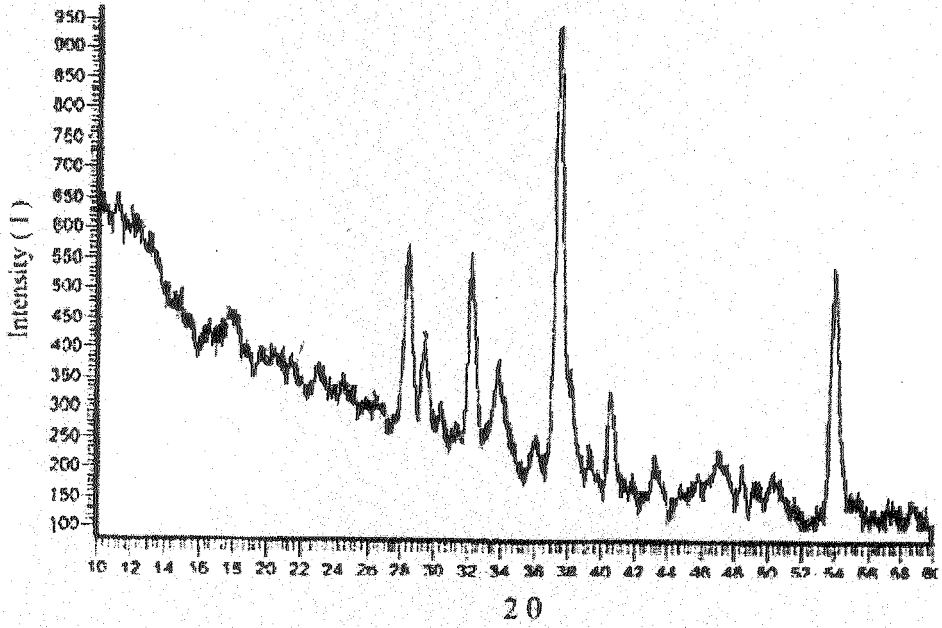

Fig. 3. The linear spectrum of the X-ray diffraction for the anode of the assembled thermal cell at 460°C

TABLE-1
A COMPARISON OF THE X-RAY DIFFRACTION VALUES FOR THE ANODE OF THE FOREIGN THERMAL CELL

d-Value for the diffraction of the component (Å)	The product	d-Value for the diffraction of the standard compound (Å)
2.624	$Ca(OH)_2$	2.628
4.98		4.90
3.113		3.112
1.921		1.927
1.793		1.796
1.688		1.687

The existence of oxidant particles in the electrolyte led to the stabilization of the generated current *via* the formation of thin layer on the anode, which activated the reaction forming the alloy, $CaLi_2$, when Ca was utilized as anode in the presence of Li^+ ions in the molten form. The formation of $Ca(OH)_2$ could be accounted for as being due to the effect of moisture during the preparation process.

Table-2 and Fig. 3 display a comparison for the X-ray diffraction values for the anode of the assembled thermal cell and the linear spectrum for this diffraction at 460°C, that is, the temperature at which the cell was operating with maximum efficiency, respectively. It has been manifested that the anode mixture included $Ca(OH)_2$, CaO and $LiCrO_2$. These findings are in excellent agreement with our previous results[9].

Additionally, Table-2 demonstrates also a comparison for the X-ray diffraction for the anode of the assembled thermal cell at 600°C, that was the temperature at which the complete consumption of the cell occurred. Fig. 4 discloses the linear spectrum for this diffraction. It is undoubtedly seen, throughout the amplitude d-values, that this electrode contained CaO, $Ca(OH)_2$ and the oxides mixture, $Li_2O{\cdot}Cr_2O_3$. No change took place upon development of compounds on the anode.

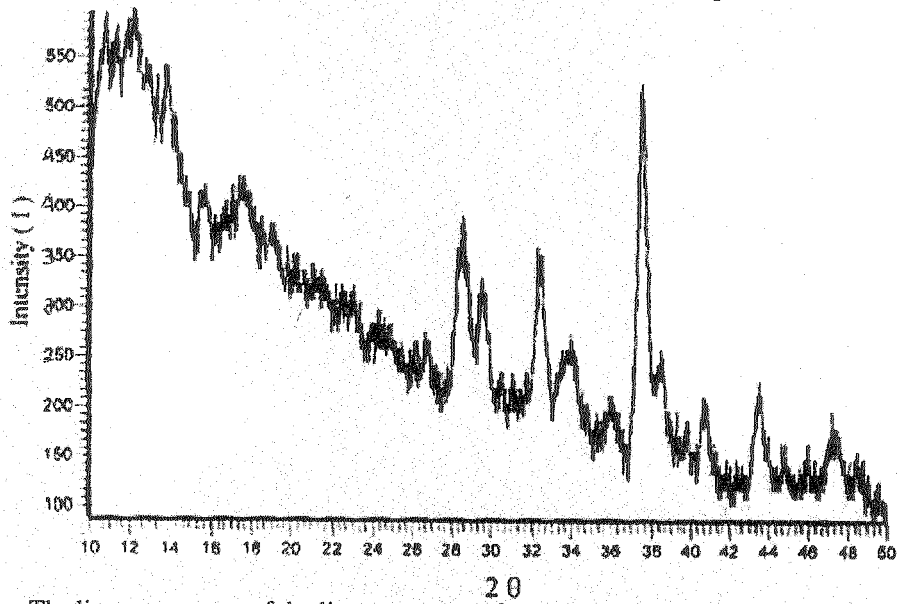

Fig. 4. The linear spectrum of the linear spectrum for the anode of the assembled thermal cell at 600°C

TABLE-2
A COMPARISON OF THE X-RAY DIFFRACTION FOR THE ANODE 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	3.144	KCl	3.146
	2.221		2.224
	2.772	CaO	2.778
	2.403		2.405
	4.989	$LiCrO_2$	4.993
	2.487		2.480
	2.355		2.350
	2.050		2.061
	3.617	$CaCrO_4$	3.620
	2.640	$Ca(OH)_2$	2.630
	4.989		4.900
	3.040	$CaCl_2$	3.050
	2.355		2.356
460	2.650	$Ca(OH)_2$	2.630
	1.935		1.930
	3.154	CaO	3.110
	2.412		2.405
	2.785		2.778
	2.701		2.701
	2.097	$LiCrO_2$	2.060
	1.880		1.890
600	2.773	CaO	2.778
	2.398		2.405
	2.639	$Ca(OH)_2$	2.630
	1.925		1.927
	3.125		3.112
	2.079	$Li_2O{\cdot}Cr_2O_3$	2.060
	2.488		2.473

It is clearly obvious that the d-values for the diffraction of the products demonstrated in Tables 1 and 2 resulting from the thermochemical reactions at the anode are in excellent agreement with those reported by ASTM for the standard analogues[7].

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