Asian Journal of Chemistry Vol. 19, No. 1 (2007), 775–780

Characterization of the Collecting Electrode in Thermal Batteries by the X-ray Technique

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

Chemistry Department, College of Science for Women, Babylon University, Iraq
E-mail: abohasan_hilla@yahoo.com

In this study, a comparison of the X-ray diffraction values for the collecting electrode of the foreign thermal cell and the linear spectrum for this diffraction, respectively, has been carried out. Two peaks belonging Ni were recognized. Additionally, a further comparison has been performed for the X-ray diffraction values of the collecting electrode component of the assembled cell and the linear spectrum for this diffraction at different temperatures. The findings demonstrate that after running the cell at 400°C the electrode embraced the compounds, NiO and KCl, beside the elemental Ni. Furthermore, a similar comparison for the collecting electrode of the assembled thermal cell at 460°C has been performed. The outcome revealed the development of two peaks for Ni as well as one peak for the emerged NiO. This indicated the incomplete oxidation of Ni, even at the maximum temperature. Finally, another comparable study for the collecting electrode, belonging to the assembled thermal cell, has been brought about at 600°C. The developed peak demonstrated the formation of NiO as the final product.

Key Words: Thermal batteries, Thermal cells, X-ray, Collecting electrode.

INTRODUCTION

A thermal battery is a high-temperature, molten-salt primary battery. At ambient temperatures, the electrolyte is a solid, non-conducting eutectic salt mixture. The thermal battery is completely inert until the electrolyte is melted. Ignition of an internal pyrotechnic heat source leads to the melting of the solid electrolyte, thus giving rise, electrochemically, to the generation of electrical power for a limited period ranging from a few seconds to 1 h. Depending on the battery's composition, thermal batteries can generate voltages of 1.5–3.3 V[1–3]. Regarding the pyrotechnic heat source, the powders of $ZrCrO_4$ and $BaCrO_4$, Fe with Mg or Al powders or $KClO_4$ represent the most prominent pyrotechnic heat

†Chemistry Department, College of Science, Ibb University, Ibb, Yemen.
‡Chemistry Department,College of Science, Kufa University, Iraq.

sources employed to activate the thermal cell[4]. The thermite mixtures are utilized either as a paper or compressed thermal disc[5–7]. The thermal paper is fabricated by employing fire mixture of Zr with $BaCrO_4$ in a precise and sufficient proportion in addition to the additives such as ceramic and asbestos[8]. The thermal paper has a great combustion rate, high heat content which approaches 1675 J g^{-1} and ignited to give inorganic ash which has a high electric resistance. Consequently, electrode collectors such as Ni or Fe and connecters among the cells should be added. Hence, the current will approach the thermal paper base in the thermal cell[5].

Regarding the identification of chemical compounds, produced from the electrochemical reaction of the thermal cell, a great importance has been directed towards this aim, using several techniques such as X-ray diffraction and thermal analyses, absorption IR spectroscopy and atomic force microscopy[9, 10]. Shembel *et al.*[9] utilized these facilities to study the physico-chemical and structural properties and the surface morphology of electrolytically produced iron sulfide compounds, which are applicable in thin-layer lithium batteries. Post-test cell examinations, conducted on Li_2FeS_2 thermal batteries[10], led to the characterization of the main electrocathodic intermediate, Li_2FeS_2. In addition, investigation of the discharged cells of high power density battery through scanning electronic microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS) allowed access to the materials distribution and layer discrimination as well as the identification of the cathodic interface, which offered an evaluation for the relation between the current density and the Li_2FeS_2 formation mechanism.

Balardi *et al.*[11] identified $La_{x-1}Sr_xMnO_3$ (X = 0, 0.20, 0.35, 0.55) compounds, which were used as the cathode material for oxide fuel cells, by using thermal analysis and XRD beside other instruments.

Ford *et al.*[12, 13] studied the amount of conversion of gamma lithium aluminate to lithium aluminate carbonate hydroxide hydrate and lithium carbonate when exposed to water vapour and carbon dioxide, by employing three techniques, *viz.*, weight gain, carbonate content and X-ray diffraction. They concluded that the reaction may involve amorphous intermediate and no one technique alone is satisfactory to investigate the conversion.

The present paper is aimed at accomplishing a comparative X-ray investigation for the collecting electrode of thermal cell 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, obtained from electrochemical reactions of the

collecting electrode in the thermal cell have been identified *via* the use of X-ray diffraction instrument. The procedure was described before[14].

Measurements were performed by using X-ray diffractometer (PW 1840, Philips). From the X-ray spectrum scheme, the amplitude d-values for the collecting electrode components were calculated by using the Bragg's equation. Because no crystalline forms with identical amplitude d-values can exist, distinguishing between crystalline materials in a sample can be accomplished 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[15].

RESULTS AND DISCUSSION

Table-1 and Fig. 1 illustrate a comparison of the X-ray diffraction values for the collecting electrode of the foreign thermal cell and the linear spectrum for this diffraction, respectively. It is undoubtedly noticed that the electrode is Ni, on the basis of the existence of two peaks belonging to Ni, where the X-ray was directed at Ni foil followed by plotting the spectrum.

TABLE-1
A COMPARISON FOR THE X-RAY DIFFRACTION FOR THE COLLECTING ELECTRODE 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)
2.064	Ni	2.034
1.781		1.762

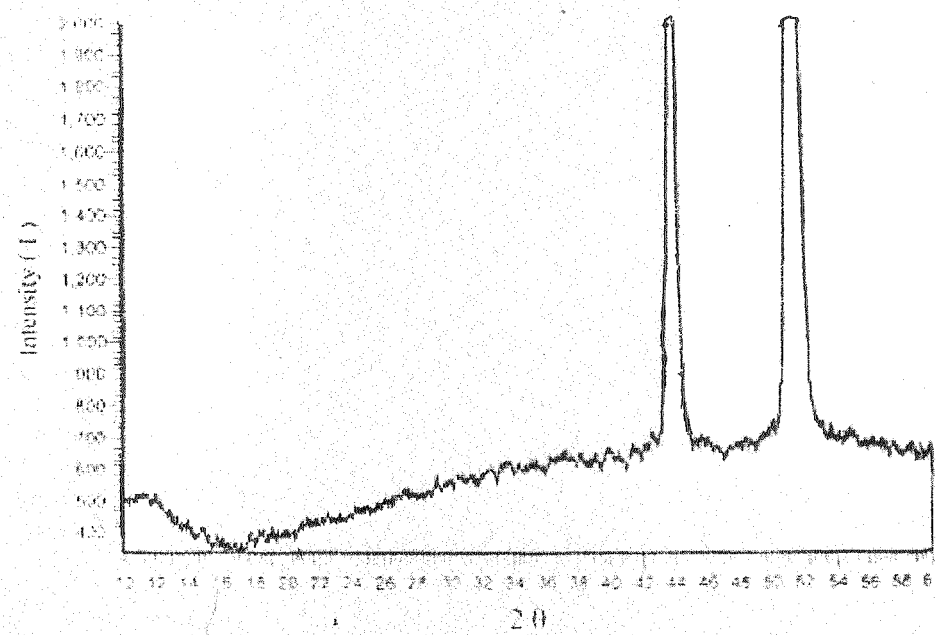

Fig. 1. Linear spectrum of the X-ray diffraction for the collecting electrode of the foreign thermal cell

Table-2 and Figs. 2–4 show a comparison for the X-ray diffraction values of the collecting electrode component of the assembled cell and the linear spectrum for this diffraction at different temperatures, *viz.*, 400, 460 and 600°C, respectively. Table-2 and Fig. 2 demonstrate obviously that after running the cell at 400°C this electrode embraced the compounds, NiO and KCl, beside the elemental Ni. In addition, the possibility of NiO formation was weak compared with that for Ni, where the temperature did not approach that required to oxidize Ni.

TABLE-2
A COMPARISON OF THE X-RAY DIFFRACTION FOR THE COLLECTING ELECTRODE OF THE ASSEMBLED THERMAL CELL AT 400°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	2.097	NiO	2.088
	2.418		2.410
	2.041	Ni	2.034
	3.170	KCl	3.150
	2.220		2.240
460	2.064	Ni	2.034
	1.787		1.782
	2.120	NiO	2.090
600	2.100	NiO	2.090
	2.430		2.410
	2.040	Ni	2.030

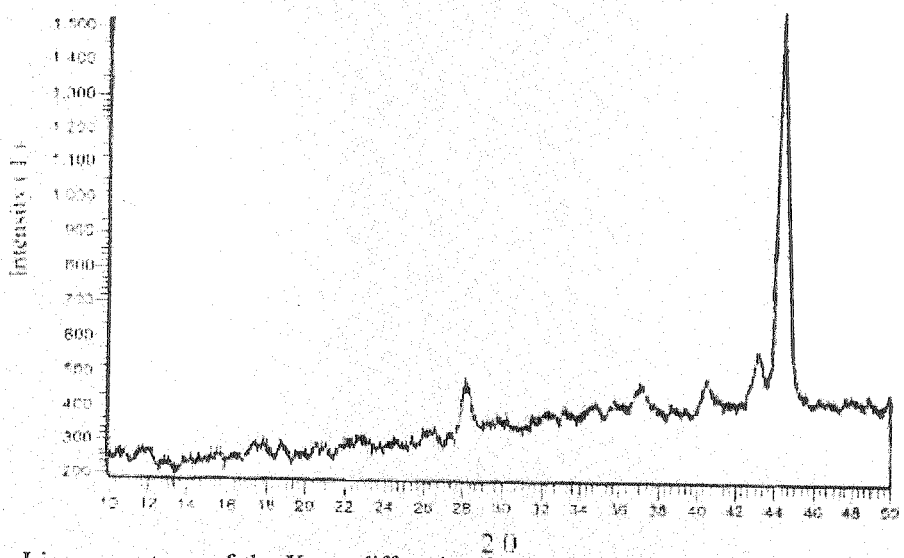

Fig. 2. Linear spectrum of the X-ray diffraction for the collecting electrode of the assembled thermal cell at 400°C

Table-2 and Fig. 3 disclose a comparison between the ray diffraction values and the linear spectrum for this diffraction, for the collecting electrode of the assembled thermal cell at 460°C, respectively. Ni developed with two peaks, while NiO emerged with one peak. This was another evidence for the incomplete oxidation of Ni, even at the maximum temperature.

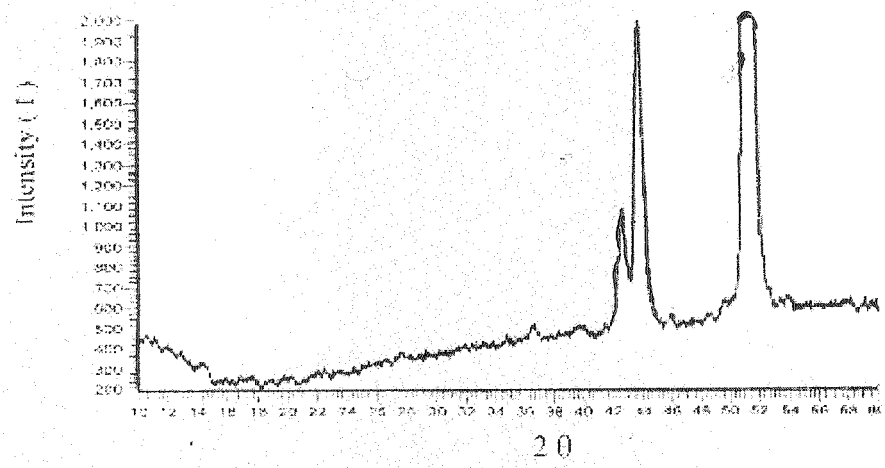

Fig. 3. Linear spectrum of the X-ray diffraction for the collecting electrode of the assembled thermal cell at 460°C

Table-2 reveals a comparison for the X-ray diffraction of the collecting electrode, belonging to the assembled thermal cell at 600°C. A peak for NiO is obviously noticed, as a final product for the thermal cell electrochemical reaction. Fig. 4 shows the diffraction spectrum for this component.

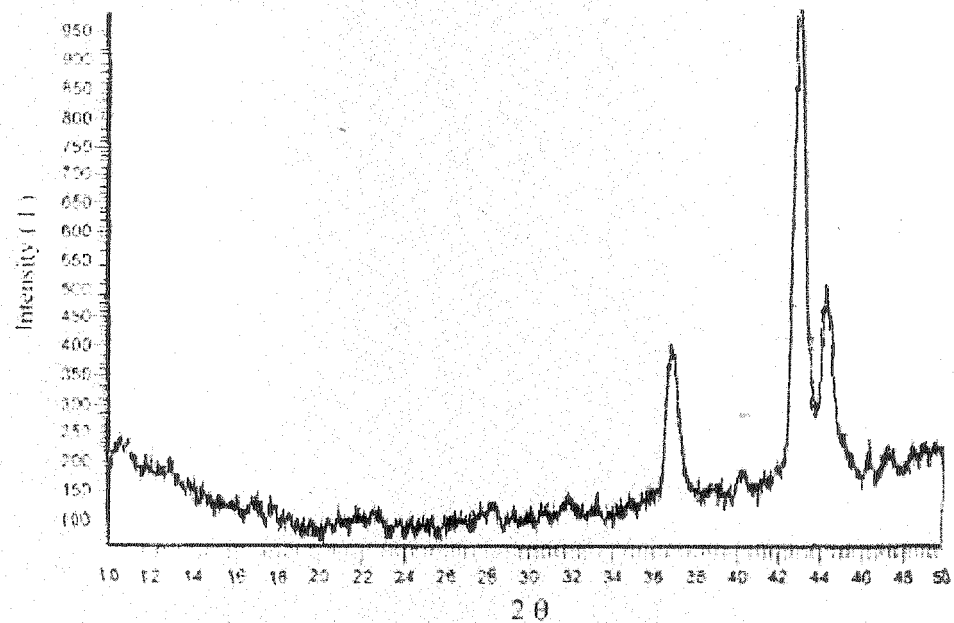

Fig. 4. Linear spectrum for the X-ray diffraction for the collecting electrode of the assembled thermal cell at 600°C

Tables 1 and 2 reveal that the d-values for the diffraction of the products, observed from the thermochemical reactions, at the collecting electrode are in good agreement with that issued by ASTM for the standard analogues[15].

REFERENCES

1. A.G. Ritchie, USA Patent 5895730 (April 20, 1999).
2. W.M. Sarhan, A.N. Alkhateeb and F.H. Hussein, *Asian J. Chem.*, **18**, 397 (2006).
3. W.J. Hamar and J.P. Sehrodt, *J. Am. Chem. Soc.*, **30**, 1090 (1949).
4. E.J. Plichta and W.K. Behl, Patent Application Department of the Army, Washington, DC, (Feb. 1990).
5. A.N. Alkhateeb, F.H. Hussein, W.M. Sarhan and K.D. Omran, *Asian J. Chem.*, **18**, 1199 (2006).
6. R. Klein, M. Menster, H.V. Elbe and B. Lewis, *J. Phys. Chem.*, **54**, 877 (1950).
7. F.H. Hussein, A.N. Alkhateeb, W.M. Sarhan and K.D. Omran, *Asian J. Chem.*, **19**, 758 (2006).
8. W.H. Collins, U.S.A. Pat. 1, 482738 (August 10, 1977).
9. E.M. Shembel, R.D. Apostolova V.M. Nagirnyi, A.S. Baskevich and P.M. Litvin, *Russ. J. Electrochem.*, **40**, 736 (2004).
10. M.J.P. Maria, M.T.C. Rupp, A.A.C. Villanova and H.M. Kohler, *Acta Microscopica*, **12**, 141 (2003).
11. R.M. Balardi, G. Francisquini, M.C. Brant, T. Matencio and R.Z. Domingues, 2nd Brazilian MRS Meeting, Symposium C, C-O2 (October 26–29, 2003).
12. S.J. Beckerman, R.B. Ford and M.T. Nemeth, Powder Diffraction, **11**, 312 (1997).
13. R.B. Ford and T.A. Taylor, Sandia National Laboratories, MRS Meeting, Symposium Y, Session - 2.7 (December 1–5, 1997).
14. F.H. Hussein, A.N. Alkhateeb, K.D. Omran and W.M. Sarhan, *Asian J. Chem.*, **19**, 765 (2007).
15. R. Jenkins and S.L Devries, An Introduction to X-ray Powder Diffractometry, N.V. Philips, Holland (1966).

(*Received*: 20 March 2006; *Accepted*: 30 June 2006) AJC-5007