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Specific Heats of $Ca_5(CrO_4)_3Cl$, Ca_2CrO_4Cl, $Ca_5(CrO_4)_3OH$, and $CaCrO_4$ at Elevated Temperatures

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The enthalpies of the Cr(V) compounds $Ca_5(CrO_4)_3Cl$ and Ca_2CrO_4Cl, and of $CaCrO_4$, were measured from 25 to 1000 °C by drop calorimetry. The corresponding properties for a third Cr(V) compound, $Ca_5(CrO_4)_3OH$, were measured from 25 to 900 °C. The specific heats at 25 °C determined from the enthalpy data are 0.180, 0.200, 0.186, and 0.194 cal/(g °C), respectively.

Introduction

The electrochemical system $Ca/CaCrO_4/Fe$ is used extensively in thermal batteries, which become functional only above the melting point of the electrolyte, typically, the LiCl–KCl eutectic, which melts at 352 °C. A study of the electrochemical reduction of $CaCrO_4$ in molten LiCl–KCl eutectic indicated the formation of $Ca_5(CrO_4)_3Cl$ as an intermediate product (*1*). In the absence of Li^+, Ca_2CrO_4Cl was formed. Because both of these materials, as well as the related Cr(V) compound $Ca_5(CrO_4)_3OH$, could be further reduced (*1*, *2*) they were considered as potential cathode materials in thermal batteries.

Thermal batteries rely upon pyrotechnic sources for raising the temperature of the battery stack to the desired operating range of 475–550 °C. For purposes of battery design and thermal modeling, it was necessary to know the specific heats of these Cr(V) compounds from room temperature to well over battery operating temperatures. Accordingly, the enthalpies and specific heats of $Ca_5(CrO_4)_3Cl$, Ca_2CrO_4Cl, and $Ca_5(CrO_4)_3OH$ were determined over a range of temperatures from 25 to 1000 °C.

Clark (*3*) has reported the specific heat of $CaCrO_4$ up to 600 °C. We also measured the enthalpy and specific heat of this common thermal battery cathode material from 25 to 1000 °C, for comparison with the Cr(V) materials and to extend the earlier data reported by Clark.

Experimental Section

Sample Preparation. $Ca_5(CrO_4)_3Cl$ and Ca_2CrO_4Cl were prepared in the manner described by Banks and Jaunarajs (*4*), except that intimate precursor mixtures of $CaCrO_4$, $CaCO_3$, and $CaCl_2$ (in the proper stoichiometric proportions) were heated under vacuum. This helped to drive the reactions to completion by removal of byproduct O_2 and CO_2. $Ca_5(CrO_4)_3Cl$ was prepared by heating the precursor mix at 750 °C for 12 h, while Ca_2CrO_4Cl was prepared by heating the precursor mix at 650 °C for 4 h. $Ca_5(CrO_4)_3OH$ was prepared by passing water-saturated argon through an intimate mixture of $Ca(OH)_2$ and $CaCrO_4$ at 900 °C for 12 h (*5*). The $CaCrO_4$ used for preparation of the Cr(V) compounds and for enthalpy measurements was 99.5% pure.

The results of product analyses are summarized in Table I. X-ray diffraction examination of the samples after calorimetric measurements showed no evidence of secondary phases resulting from thermal decomposition.

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Table I. Analysis of Cr(V) Compounds[a]

compd	Ca	Cr	Cl	O	phases[b]
$Ca_5(CrO_4)_3Cl$	34.3	26.2	5.90	36.5 ± 1.8	$Ca_5(CrO_4)_3Cl$
theor[c]	34.32	26.72	6.07	32.90	
Ca_2CrO_4Cl	34.8	22.2	15.1	29.0 ± 1.5	Ca_2CrO_4Cl
theor[c]	34.61	22.45	15.31	27.63	
$Ca_5(CrO_4)_3OH$	35.60	27.30			$Ca_5(CrO_4)_3OH$
theor[c]	35.44	27.59		36.79	

[a] Composition is in weight percent. [b] Identified by X-ray diffraction analysis. [c] Theoretical.

Table II. Experimental Enthalpy of $Ca_5(CrO_4)_3Cl$ as a Function of Temperature[a]

temp, °C	*H*, cal/g	temp, °C	*H*, cal/g	temp, °C	*H*, cal/g
25[b]	0.0	400	72.9	801	162.5
106	14.7	480	93.8	852	177.5
195	33.0	588	115.3	898	188.7
212	35.3	668	133.1	906	190.0
285	51.6	704	142.0	954	202.4
288	48.8	756	155.2	998	215.3

[a] 1 cal (thermochemical) = 4.1840 J. [b] Reference temperature.

Table III. Experimental Enthalpy of Ca_2CrO_4Cl as a Function of Temperature[a]

temp, °C	*H*, cal/g	temp, °C	*H*, cal/g	temp, °C	*H*, cal/g
22[b]	0.0	432	82.7	737	148.5
118	19.3	489	92.7	739	149.0
209	36.5	552	107.4	846	174.0
321	59.8	600	116.6	867	178.9
324	61.8	635	127.0	904	190.8
400	75.9	726	145.7	947	200.0

[a] 1 cal (thermochemical) = 4.1840 J. [b] Reference temperature.

Calorimetric Measurements. The powdered samples were sealed under vacuum in platinum capsules by electron-beam welding. Typical sample masses were 4–6 g. Enthalpy measurements were made with a liquid argon vaporization calorimeter, described by Roth (*6*). The calorimeter was calibrated with a known electrical heat input and NBS standards to within ±1% accuracy. The samples were heated in an isothermal tube furnace, and the sample temperature was determined with a thermocouple calibrated to within ±0.3% by using IPTS 68. Temperature gradients within the furnace were verified to be less than 1 °C.

The enthalpy data were curve fitted by using a third-order B-spline routine (*7*). A typical enthalpy–temperature plot is shown in Figure 1 for $Ca_5(CrO_4)_3OH$. The curve fit to the enthalpy data was differentiated with respect to temperature to obtain the corresponding specific heat function. When all experimental errors and mathematical uncertainties associated with the curve fitting and differentiation are considered, the specific heat data are accurate to within ±5%.

Results

The enthalpy data for the Cr(V) compounds and $CaCrO_4$ are summarized in Tables II–V as a function of temperature. The enthalpy data were referenced to room temperature for each measurement series, as given by the first temperature listed in

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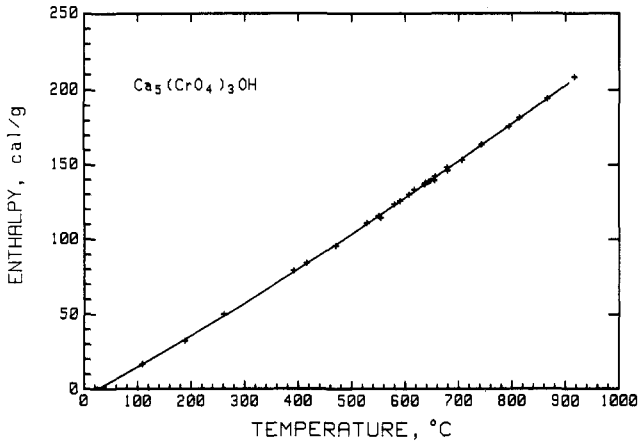

Figure 1. Typical enthalpy vs. temperature data for the material $Ca_5(CrO_4)_3OH$. All enthalpy data are referenced to room temperature, as indicated in the tables. The solid line is the curve fit to the experimental data.

Table IV. Experimental Enthalpy of $Ca_5(CrO_4)_3OH$ as a Function of Temperature[a]

temp, °C	H, cal/g	temp, °C	H, cal/g	temp, °C	H, cal/g
25[b]	0.0	554	114.4	656	142.1
109	16.8	580	123.5	679	148.1
189	32.3	590	125.6	679	145.9
260	50.0	607	129.9	707	153.0
391	79.0	617	133.1	744	163.6
415	84.1	637	136.8	795	175.8
469	95.6	638	137.6	815	181.7
528	110.9	645	138.7	866	194.4
550	115.6	648	139.2	916	208.3
		655	139.4		

[a] 1 cal (thermochemical) = 4.1840 J. [b] Reference temperature.

Table V. Experimental Enthalpy of $CaCrO_4$ as a Function of Temperature[a]

temp, °C	H, cal/g	temp, °C	H, cal/g	temp, °C	H, cal/g
22[b]	0.0	245	43.3	692	143.90
68	8.6	301	54.4	790	166.6
112	16.9	392	74.8	849	181.8
132	20.6	488	96.5	888	191.2
178	29.4	491	97.4	986	217.2
		591	120.3		

[a] 1 cal (thermochemical) = 4.1840 J. [b] Reference temperature.

Table VI. Polynomial Coefficients for Curve Fits to Specific Heat[a] Data

coeff	$Ca_5(CrO_4)_3Cl$	Ca_2CrO_4Cl	$Ca_5(CrO_4)_3OH$	$CaCrO_4$
A	1.771×10^{-1}	2.013×10^{-1}	1.909×10^{-1}	1.813×10^{-1}
B	1.050×10^{-4}	-3.323×10^{-5}	1.219×10^{-4}	1.084×10^{-4}
C	-3.466×10^{-8}	1.016×10^{-7}	-5.530×10^{-8}	-3.341×10^{-8}

[a] C_p (cal/(g °C)) = $A + BT + CT^2$ (T in °C).

each table. The mathematical expressions that describe the specific heat–temperature relationships are listed in Table VI. No thermal anomalies were evident for any of these materials. The specific heats for the three Cr(V) compounds are comparable and similar to that for $CaCrO_4$, which is a standard thermal-battery cathode material.

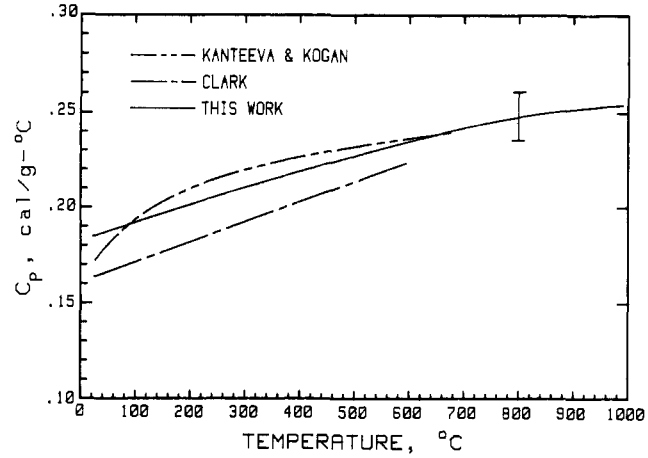

Figure 2. Specific heat curves for the reference material $CaCrO_4$. Data from this work are compared to those of Clark and the calculated values of Kanteeva and Kogan.

The specific heat of $CaCrO_4$ determined in this study is compared in Figure 2 with the experimental data of Clark (*3*) and calculated data of Kanteeva and Kogan (*8*). Our specific heat data are intermediate between those of Clark and Kanteeva and Kogan. The accuracy of our data is indicated by the error bar.

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Registry No. $Ca_5(CrO_4)_3Cl$, 12013-87-5; Ca_2CrO_4Cl, 12013-58-0; $Ca_5(CrO_4)_3OH$, 12013-89-7; $CaCrO_4$, 13765-19-0.

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