

# A comparative study of the thermal stability of $\text{Li}_{1-x}\text{CoO}_2$ and $\text{Li}_{3-x}\text{CrMnO}_5$ in the presence of 1 M $\text{LiPF}_6$ in 3:7 EC/DEC electrolyte using accelerating rate calorimetry

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## Abstract

A comparative study of the thermal stability of charged cathodes, by accelerating rate calorimetry, found that cathodes based on  $\text{Li}_3\text{CrMnO}_5$  were less thermally reactive with a conventional electrolyte solution, 1 M  $\text{LiPF}_6$  in 3:7 EC/DEC, than cathodes containing  $\text{LiCoO}_2$ . Arrhenius parameters of activation energies and frequency factors were determined from forced heating experiments. The exothermic reactions of  $\text{Li}_3\text{CrMnO}_5$  cathodes were investigated as a function of state of charge, electrolyte solution volume and electrolyte salt concentration.

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## 1. Introduction

This paper reports on the results obtained from a comparative accelerating rate calorimetry study on a proposed alternative cathode material,  $\text{Li}_3\text{CrMnO}_5$  [1] versus the current most commonly used material,  $\text{LiCoO}_2$ . The experimental procedures for using accelerating rate calorimetry for the analysis of the thermal stability of lithium ion battery materials were developed by researchers at MoliEnergy Ltd. (1990) [2] and later refined for smaller samples by Richard and Dahn [3]. Following the procedure developed by Richard and Dahn [3], the Arrhenius parameters of activation energies and frequency factors for the initial reactions of  $\text{LiCoO}_2$  and  $\text{Li}_3\text{CrMnO}_5$  cathodes with 1 M  $\text{LiPF}_6$  in 3:7 EC/DEC electrolyte were determined from experiments in which the samples were heating to a range of initial temperatures above the onset temperature for reaction. In addition, the exothermic reactions of  $\text{Li}_3\text{CrMnO}_5$  cathodes were investigated as a function of state of charge, electrolyte solution volume and electrolyte salt concentration.

A study of the decomposition reactions was conducted for the  $\text{Li}_3\text{CrMnO}_5$  cathodes by quenching the exothermic reactions at different points and obtaining X-ray diffraction

patterns of the partially reacted solids and by extracting organic residues for chromatographic analysis.

## 2. Experimental

The  $\text{Li}_3\text{CrMnO}_5$  was prepared by reacting stoichiometric quantities of a double hydroxide of chromium and manganese, prepared by co-precipitation, with lithium carbonate at 800 °C for 8 h in an inert gas atmosphere. The sample of  $\text{Li}_3\text{CrMnO}_5$  used for this study had a surface area of 5.5 m<sup>2</sup> g<sup>-1</sup> as measured by the BET technique. Commercial  $\text{LiCoO}_2$  (Seimi) with a BET of 0.4 m<sup>2</sup> g<sup>-1</sup> was used for the comparative studies. Electrode material was prepared by combining, by mass, 76% active material, 8% carbon black (Ensagri), 8% graphite (Lonza KS-4), and 8% binder (KynarFlex 2801-F). After thoroughly mixing the components to form a uniform paste, the mixture was dried in a convection oven at 60 °C. The dried electrode material was then ground into a fine, homogenized powder, placed into a glass sample bottle and stored in an oven at 60 °C until needed. The cathodes were prepared by weighing 200–225 mg of the electrode mixture into a clean stainless steel die and compressing to 1.25 t for 30 s in a hydraulic press. Test cells were assembled in 2325 coin cell hardware in a glove box under an argon atmosphere. Metallic lithium disks of 1.65 cm diameter and 0.05 cm thickness were used for the

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anodes. Two 2 cm diameter layers of separator: one of glass fiber (Whatman) and one of microporous polypropylene (Celgard 3501) and 100  $\mu\text{l}$  of 1 M  $\text{LiPF}_6$  in 3:7 (w/w) EC/DEC (Mitsubishi Chemical) electrolyte completed the cell.

The coin cells were cycled at currents of 1.5 mA  $\text{g}^{-1}$  of active material mass to the designated limiting voltages. The  $\text{LiCoO}_2$  cells were charged once to 4.2 V while the  $\text{Li}_3\text{CrMnO}_5$  cells were charged to the limiting voltage, discharged to 2.5 V and charged again to the same limiting voltage as the first charge. In separate experiments, limiting voltages of 4.2–4.5 V were explored for the  $\text{Li}_3\text{CrMnO}_5$  cells. When cycling was complete, the cells were transferred to a helium atmosphere glove box for careful disassembly such that shorting was prevented. The cycled cathode pellet was recovered and placed into an agate mortar and pestle where it was ground lightly to a uniformly powder form. This powder was quantitatively transferred to a waiting 2.5 cm long, acetone washed, stainless steel tube (the bomb) that had been previously welded shut at one end. Once the cycled cathode powder was in the tube, a mass of electrolyte (1 M  $\text{LiPF}_6$  in 3:7 EC/DEC) equivalent to mass of active material in the electrode was carefully transferred by pipette onto the powder. In most instances, the cycled cathode material was washed, in advance of being loaded into the tube, with three aliquots of 700  $\mu\text{l}$  of dimethyl carbonate (DMC). The washed samples were centrifuged and the DMC decanted off between aliquots in order to remove the excess salt, then dried in the anti-chamber of the glove box prior to adding the sample to the bomb and adding the fresh electrolyte. Before removing the filled tubes from the glove box, an airtight crimp was formed on the open end. The tubes were then quickly welded shut outside of the glove box in a chilled brass block heat sink that served to prevent heating of the samples.

For the state of charge experiments, the calorimeter was programmed to heat to an initial temperature of 50  $^\circ\text{C}$  and then enter into a heat–wait–search mode of operation. In this mode, the calorimeter heated in increments of 10  $^\circ\text{C}$  at a rate of 5  $^\circ\text{C min}^{-1}$ , waited for 15 min at each temperature increment, and then searched for heat evolved at a rate  $>0.02$   $^\circ\text{C min}^{-1}$  for 10 min. If such a condition was detected, the calorimeter “tracked” the exothermic activity adiabatically by maintaining the zone temperatures (top, bottom, and sides) at the current temperature detected by the bomb thermocouple until the temperature evolution rate fell below the user-programmed threshold of 0.02  $^\circ\text{C min}^{-1}$ . This process continued until the upper temperature set point (300  $^\circ\text{C}$ ) had been reached.

For the studies of the effect of increasing the initial self-heat rate, the calorimeter was heated to a temperature set point greater than the initial reaction temperature detected during the full temperature range scans. Once the set point had been reached the calorimeter immediately performed a 10 min search for a temperature increase greater than the threshold rate.

In the study of the intermediate decomposition products, the calorimeter was programmed to initially heat to 20  $^\circ\text{C}$  below the temperature, where the sustained reactions were observed in the full range scans and then to enter into the typical heat–wait–search mode. The calorimeter was also programmed to stop heating and air cooled after interesting exothermic events. These were characterized as minima in the self-heat rate plots as seen on full range scans. After the calorimetry experiment, the bombs were then transported to a glove box where they were cut open with a tube cutter near the center of the bomb. The powder residue was quantitatively transferred to a centrifuge tube and washed with three 700  $\mu\text{l}$  aliquots of fresh DMC. After centrifuging at 12,000 rpm for 30 s, the DMC extracts were collected with a pipette and combined in a clean sample vial.

The extracted residual solids were then dried in the glove box anti-chamber and after drying were ground to a fine powder and stored in clean sample vials in the glove box until X-ray diffraction patterns could be obtained.

### 3. Results and discussion

Plots of the initial self-heating rate as the logarithm of the change in temperature divided by the change in time,  $\log dT/dt$ , versus temperature for  $\text{Li}_3\text{CrMnO}_5$  cathodes charged to 4.3 V, are shown in Fig. 1, for initial temperatures ranging from 189 to 210  $^\circ\text{C}$ . These data were used to calculate the Arrhenius parameters, activation energy,  $E_a$ , and frequency factor,  $A$ , following the methods of Richard and Dahn [3]. Re-plotting the data for the  $\text{Li}_3\text{CrMnO}_5$  cathodes, and from an analogous series of experiments for  $\text{LiCoO}_2$  charged to 4.2 V, as the natural logarithm,  $\ln(dT/dt)$ , versus the inverse of temperature,  $1/T$ , shown in Fig. 2, allows the calculation

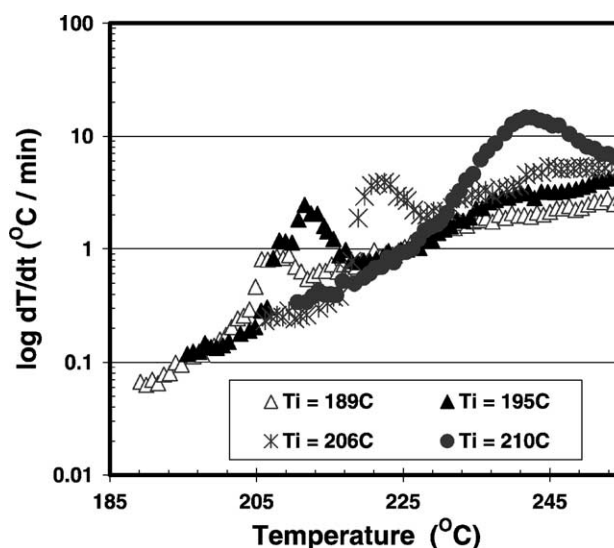


Fig. 1. Plots of initial self-heating rate vs. temperature for  $\text{Li}_3\text{CrMnO}_5$  cathodes charged to 4.3 V after heating to initial temperatures: 189, 195, 206 and 210  $^\circ\text{C}$ .

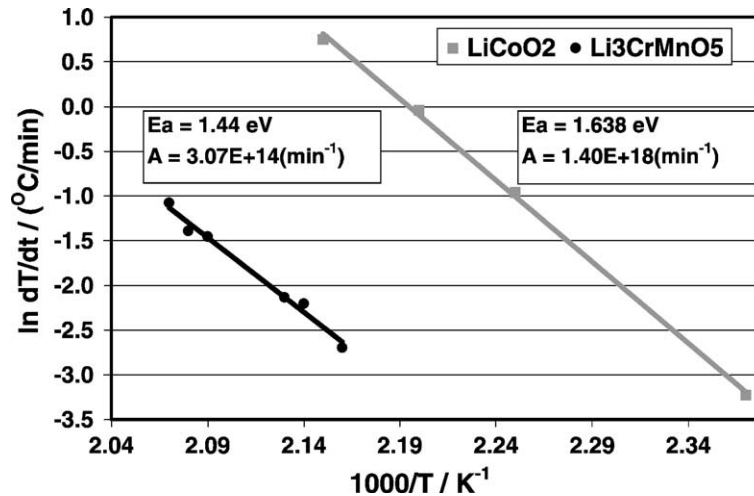


Fig. 2. Arrhenius plots for the initial reaction of electrolyte solutions containing 1 M LiPF<sub>6</sub> in 3:7 EC/DEC with LiCoO<sub>2</sub> and Li<sub>3</sub>CrMnO<sub>5</sub> cathodes charged to 4.2 and 4.3 V, respectively.

of activation energies and frequency factors from the slopes and intercepts, respectively, according to the equation:

$$\ln\left(\frac{dT}{dt}\right) \approx \ln(A\Delta T) - \frac{E_a}{k_\beta T},$$

where  $\Delta T$  is the temperature change of the sample caused by the reactants and  $k_\beta$  the Boltzmann's constant.

The close agreement between the Arrhenius parameters determined in this study for LiCoO<sub>2</sub> cathodes with previously published results from MacNeil et al. [4] validated the experimental procedures. From the summary of the study of the effect of increasing the initial temperature in Table 1, it can be determined that even though the LiCoO<sub>2</sub> cathodes were of much lower surface area and at a much lesser depth of charge, about 150 mAh g<sup>-1</sup> versus over 200 mAh g<sup>-1</sup> for the Li<sub>3</sub>CrMnO<sub>5</sub> cathodes, they exhibited greater thermal instability than the charged cathodes containing Li<sub>3</sub>CrMnO<sub>5</sub>. Although the activation energies only differed slightly, the frequency factor for the reaction with the LiCoO<sub>2</sub> cathodes

indicated that the reaction occurred at a much faster rate. The enthalpy per unit time for the two reactions also indicated that the charged LiCoO<sub>2</sub> cathodes were more thermally unstable than those of Li<sub>3</sub>CrMnO<sub>5</sub> as the energy produced from the reactions was evolved at a rate approximately 1.5 times faster. The heat capacities of the two systems were comparable, however, that of the charged Li<sub>3</sub>CrMnO<sub>5</sub> cathodes was slightly greater. Additionally, the maximum self-heat rate for the Li<sub>3</sub>CrMnO<sub>5</sub> was found to be, in most cases, significantly lower, four times in the case of an initial temperature of 190 °C, than for the LiCoO<sub>2</sub> cathodes. Another interesting feature observed for the Li<sub>3</sub>CrMnO<sub>5</sub> experiments was a long steady lead up time to the initiation of the portion of the reaction that produced the largest quantity of heat. When the samples were heated to an initial temperature of 150 °C, it was observed that there was a 400-min "wait" time before the extensive heat production occurred for charged Li<sub>3</sub>CrMnO<sub>5</sub> cathodes, whereas, the LiCoO<sub>2</sub> cathodes went immediately into a rapid self-heating.

Table 1  
Summary for initial temperature experiments for LiCoO<sub>2</sub> and Li<sub>3</sub>CrMnO<sub>5</sub> cathodes

Initial temperature (°C)	Self-heat rate (max) (°C min <sup>-1</sup> )	Capacity (mAh g <sup>-1</sup> )	C <sub>TOT</sub> (J K <sup>-1</sup> )	Time to elevated rate (min)	E <sub>a</sub> (eV)	A (min <sup>-1</sup> )
<b>LiCoO<sub>2</sub></b>						
150	1	147	1.397	0	1.64	1.40E + 18
170	9	142	1.331	0		
170	10	151	1.392	0		
180	30	151	1.357	0		
190	80	151	1.358	0		
<b>Li<sub>3</sub>CrMnO<sub>5</sub></b>						
150	1.6	207	1.406	400	1.44	3.07E + 14
189	6	221	1.414	138		
193	7	219	1.411	113		
195	17	221	1.414	70		
206	17	220	1.400	41		
210	20	226	1.405	36		

Table 2  
Summary for state of charge experiment for LiCoO<sub>2</sub> and Li<sub>3</sub>CrMnO<sub>5</sub> cathodes

Charge limit (V)	Accumulated capacity (mAh g <sup>-1</sup> )	Total heat capacity (J K <sup>-1</sup> )	Total ΔT (K)	Total ΔH (J)	Total ΔH (J g <sup>-1</sup> )	Total ΔH/t (J (g min) <sup>-1</sup> )
LiCoO <sub>2</sub>						
4.2	149.9	1.3976	110	153.7	890	1.48
Li <sub>3</sub> CrMnO <sub>5</sub>						
4.2	200.6	1.4050	120	168.6	998	0.80
4.3	207.4	1.4059	130	182.8	1075	0.86
4.4	239.2	1.3913	134	186.4	1090	0.97
4.5	255.1	1.4118	130	183.5	1070	0.98

Further to the comparative initial temperature experiments that were conducted for both LiCoO<sub>2</sub> and Li<sub>3</sub>CrMnO<sub>5</sub>, additional thermal studies were conducted on Li<sub>3</sub>CrMnO<sub>5</sub> cathodes, which evaluated the effects of varying the state of charge, the electrolyte volume, and the salt concentration. Table 2 summarizes the results for additional thermal studies on Li<sub>3</sub>CrMnO<sub>5</sub> cathodes as a function of varying their state of charge. Not surprisingly, it was found that as the limiting charge voltage was increased the thermal stability of the system decreased. A rapid increase in the self-heat rate of the first thermal event was observed as the material was charged beyond 4.4–4.5 V. This was attributed to a secondary reaction pathway being accessed in the deeply charged cathodes at or around the decomposition temperature (190 °C) of the electrolyte.

A plot of the self-heating rate versus temperature of Li<sub>3</sub>CrMnO<sub>5</sub> cathodes charged to 4.3 V as a function of the mass ratio of electrolyte solution to active mass is shown in Fig. 3. It was observed that when the electrolyte volume to active mass ratio was increased, the first primary thermal event became more intense while the second event demonstrated a decreased self-heating rate. This effect is most likely attributable to the formation of a reaction product between the active material and the electrolyte salt that

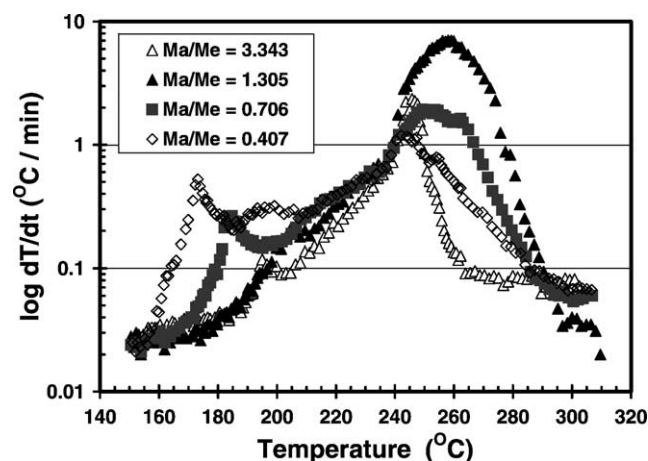


Fig. 3. Plot of self-heating rate vs. temperature as a function of the mass ratio of charged Li<sub>3</sub>CrMnO<sub>5</sub> cathode material ( $M_a$ ) to added electrolyte solution ( $M_c$ ).

effectively insulates the solid from reacting with the organic portion of the electrolyte. The total enthalpy change, however, remained similar for the system as different volumes of electrolyte were added.

The greatest effect on the enthalpy was obtained for the electrolyte salt concentration experiment as can be seen in Table 3. When the concentration of the salt was increased to the point of saturation it was found that the initial thermal event increased in self-heat rate significantly from <1 to over 10 °C min<sup>-1</sup>. The second major thermal event remained more or less unchanged.

This when taken into consideration with the state of charge and the electrolyte volume experiments implied that the first primary event was associated with a solid–electrolyte salt interaction while the second event was most associated with the decomposition of the organic portion of the electrolyte. This was further evidenced by the GC–FID analysis that was performed on the ARC residues. This analysis indicated that the organic portion was mostly decomposed by 245 °C. In this region, there was about an 80% reduction of the quantity of extractable organic residue.

The X-ray diffraction patterns that were obtained on the solid residues from the ARC experiments indicated that the crystal structure of Li<sub>3</sub>CrMnO<sub>5</sub> was mostly maintained until 245 °C. In solid residues that had been heated above 245 °C, significant changes were observed in the diffraction patterns as large reductions in the peak intensities were accompanied by peak broadening and shifts toward lower  $2\theta$  values.

DMC extracted cycled cathode material was found to be less reactive than active material that was not washed after

Table 3  
Summary of the effect of varying the salt concentration on the thermal stability of Li<sub>3</sub>CrMnO<sub>5</sub> cathodes charged to 4.3 V

Concentration (M)	Total heat (J K <sup>-1</sup> )	ΔT (K)	ΔH (J)	ΔH (J g <sup>-1</sup> active)
0.50	1.2271	66	81.0	513.0
0.75	1.2450	76	94.6	627.3
1.00	1.2560	66	82.9	729.8
1.25	1.2472	92	114.7	730.1
2.25	1.2700	104	132.1	890.2

cycling. This was attributable to the increase in the effective salt concentration.

#### 4. Conclusions

The relative thermal stability of  $\text{Li}_3\text{CrMnO}_5$  cathodes with a conventional electrolyte solution was compared to that of  $\text{LiCoO}_2$  cathodes by accelerating rate calorimetry. The activation energies and frequency factors determined from forced heating experiments were found to be 1.638 eV and  $1.40E + 18 \text{ min}^{-1}$  for  $\text{LiCoO}_2$  and 1.44 eV and  $3.07E + 14 \text{ min}^{-1}$  for  $\text{Li}_3\text{CrMnO}_5$ , respectively. The heat capacity of the  $\text{Li}_3\text{CrMnO}_5$  cathodes was, on average, slightly larger than for  $\text{LiCoO}_2$ ,  $1.411 \text{ J K}^{-1}$  as compared to  $1.376 \text{ J K}^{-1}$ .

The total enthalpy for the reaction of charged  $\text{Li}_3\text{CrMnO}_5$  cathodes with the electrolyte solution was about 1.2 times greater than for  $\text{LiCoO}_2$ , while the energy change per unit mass per unit time was about 1.7 times greater in the case of  $\text{LiCoO}_2$ . The maximum self-heat rate for  $\text{LiCoO}_2$  cathodes charged to 4.2 V was observed to be similar to the maximum self-heat rate for those of  $\text{Li}_3\text{CrMnO}_5$  charged to 4.3 V, however, the  $\text{LiCoO}_2$  cathodes produced the heat at a much

faster rate. The reaction between charged  $\text{Li}_3\text{CrMnO}_5$  cathodes and the electrolyte solution was found to be dependent on both the volume of the additional electrolyte added and the concentration of the electrolyte salt. The reactivity of the system increased with increasing salt concentration and with increasing ratio of electrolyte solution to cathode mass.

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