

Differential scanning calorimetry material studies: implications for the safety of lithium-ion cells

Z. Zhang^{*}, D. Fouchard, J.R. Rea

Rayovac Corporation, Madison, WI 53711, USA

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Abstract

Differential scanning calorimetry (DSC) has been demonstrated to be a useful means of studying the reactivity of materials used in lithium-ion cells. In the present study, the reactivity of three most commonly used transition metal oxides, i.e. Li_xNiO_2 , Li_xCoO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, in the presence of electrolyte were investigated by DSC. The most commonly used negative electrode material, carbon (Li_xC_6) was also studied. In the paper, relative levels of reactivity of the materials as a function of stoichiometry are reported. The implications of the results on the safety of lithium-ion cells are discussed. © 1998 Elsevier Science S.A.

Keywords: Lithium-ion batteries; Safety; Differential scanning calorimetry; Reactivity

1. Introduction

Lithium-ion technology using lithium transition metal oxide positives and carbon negatives is rapidly becoming the state-of-the-art rechargeable battery technology. A unique combination of high voltage, high energy density, excellent cycle life and moderate rate capability has made the Li-ion cell one of the leading power sources for a wide range of portable electronics applications [1]. The technology also shows promise for eventual electric-vehicle applications.

Although the replacement of metallic Li with carbon intercalation negatives significantly improved the safety of secondary Li cells, some concerns remain, particularly in view of recent problems in the field [2]. Li-ion cells are not immune to safety incidents since their thermal stability limits are finite. We have found that cells deliberately heated to high temperatures eventually undergo a thermal runaway reaction, producing very high cell temperatures, smoke and even fire [3]. This implies that under abusive conditions, the potential exists to heat a cell beyond its thermal stability limit, initiating the runaway reaction and producing a safety incident. To date, safety engineering has played a key role in mitigating potential safety prob-

lems. Techniques such as precise charge control, internal fusing and over-pressure disconnect devices have been quite successful in achieving battery safety.

From a materials point of view, the safety characteristics intrinsically depend on the stoichiometry of the metal oxide electrodes and carbon electrodes (x in Li_xNiO_2 and Li_xC_6 for example). The x values in the three most commonly used metal oxide materials, i.e. Li_xNiO_2 , Li_xCoO_2 and $\text{Li}_x\text{Mn}_2\text{O}_4$, have been found to have significant impact on their thermal stability at high temperatures. Thermal gravity analysis (TGA) studies of electrolyte-free Li_xNiO_2 , Li_xCoO_2 and $\lambda\text{-MnO}_2$ samples have been reported [4], where small x values encouraged the decomposition of the active materials with the liberation of O_2 . Even though the carbon intercalation electrode is much safer than Li metal [5], it still can react with the electrolyte and generate heat under abusive conditions, especially for large x values in Li_xC_6 .

In practical cell operation, both the positive and negative electrode will undergo reactions with the electrolyte if the cell is abused. Although many companies have reported results of cell safety evaluations, data on the anode and cathode intrinsic safety properties, and their reaction mechanisms with the electrolyte have been sparse. Because of the exothermic nature of the reactions, differential scanning calorimetry (DSC) offers a convenient means of studying the reaction rates and mechanisms under controlled conditions. With this technique, samples are heated

^{*} Corresponding author: Tel.: 608-275-4776; Fax: 608-275-4992.

at a controlled rate, and the heat flow to or from the sample is measured. By comparing heat flow rates, onset temperatures and total heat generation, the effects of variables such as electrode materials, stoichiometry and electrolyte compositions on cell safety can be readily studied.

The present DSC investigation deals with the intrinsic reactivity of Li_xNiO_2 , Li_xCoO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, and Li_xC_6 at different x values in the presence of the electrolyte. The understanding of such reactions is essential in the design of safe, high performance Li-ion cells.

2. Experimental

LiNiO_2 was obtained from FMC, LiCoO_2 from Fuji and LiMn_2O_4 from Chemetals. The MCMB25-28 (meso-carbon microbeads, average particle size of 25 μm , graphitized at 2800 $^\circ\text{C}$) carbon material was purchased from Osaka Gas. Electrodes were made by slurry-coating on aluminium or copper substrates. All electrodes used polyvinylidene fluoride (PVDF) binder (Elf Atochem). Unless noted otherwise, the electrolyte used in the study was 1.0 M LiPF_6 (Hashimoto) in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 by volume). Both EC and DMC were obtained from Grant Chemical.

Sample preparation initially consisted of de-intercalation of LiNiO_2 , LiCoO_2 , or LiMn_2O_4 electrodes, or intercalation of carbon electrodes. This was carried out in 2325 coin cell hardware using an Li metal foil as the counter electrode at a current density of 0.1 mA/cm^2 . The cells were either charged (metal oxide samples) or discharged (carbon samples) to a predetermined capacity to achieve the desired stoichiometry for the materials under study. Voltage cutoffs were also used (5.0 V for cathode materials, 0.01 V for anode materials) to ensure that only intercalation reactions occurred during the sample preparation.

The coin cells were then transferred to a glove box containing an argon atmosphere, and opened. About 0.5–1.5 mg of the active materials of interest was taken, placed in aluminum DSC cells and hermetically sealed by crimping. The Li metal and separator were discarded. Unless otherwise noted, all the lithiated oxide samples had 16–26 wt.% electrolyte and the carbon samples had ~ 30 wt.% electrolyte. All DSC calculations were based on the overall weight of the sample. The DSC experiments were carried out on a Model DSC10 differential scanning calorimeter (TA Instruments) at a ramp rate of 10 $^\circ\text{C}/\text{min}$. The temperature range utilized was from room temperature to 400 $^\circ\text{C}$. Exothermic and endothermic reactions as a function of the temperature were plotted as positive and negative heat flow, respectively.

3. Results and discussion

The stoichiometric values of lithium nickelate, cobaltate, manganate and MCMB25-28 carbon covered in the

Table 1

Summary of material stoichiometry values for DSC tests, x values in the indicated compounds

Material	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Li_xNiO_2	1.0	0.75	0.45	0.35	0.25	0.05
Li_xCoO_2	1.0	0.75	0.45	0.35	0.25	0.014
$\text{Li}_x\text{Mn}_2\text{O}_4$	1.0	0.46	0.20	0.11		
Li_xC_6	0	0.23	0.46	0.91		

present studies are summarized in Table 1. Fig. 1 shows the DSC curves of Li_xNiO_2 plus the electrolyte for x values of 1.0 to 0.05. The LiNiO_2 was quite stable over the entire temperature range, and only a small endothermic peak from 250 to 280 $^\circ\text{C}$ was observed. This appeared to be due to electrolyte endothermic reactions. Scans on solid LiPF_6 and the electrolyte both produced endothermic peaks in this temperature range. As the x values of the Li_xNiO_2 decreased, a gradual increase in reactivity was observed. A highly exothermic reaction occurred with $x \leq 0.25$ having an onset temperature around 200 $^\circ\text{C}$. To determine if the reaction was the result of oxidation reactions between the delithiated nickel material and the electrolyte rather than a simple decomposition of the Li_xNiO_2 material, a sample of $\text{Li}_{0.25}\text{NiO}_2$ was washed several times in DMC and vacuum-dried prior to analysis. Fig. 2 compares $\text{Li}_{0.25}\text{NiO}_2$ with and without the washing/vacuum-drying procedure. It can be seen that the washing/vacuum-drying procedure reduced the exothermic energy significantly, from 1256 to 146 J/g. When electrolyte was reintroduced to the sample, the reactivity returned to its original value, confirming that the electrolyte was involved in the reaction. When

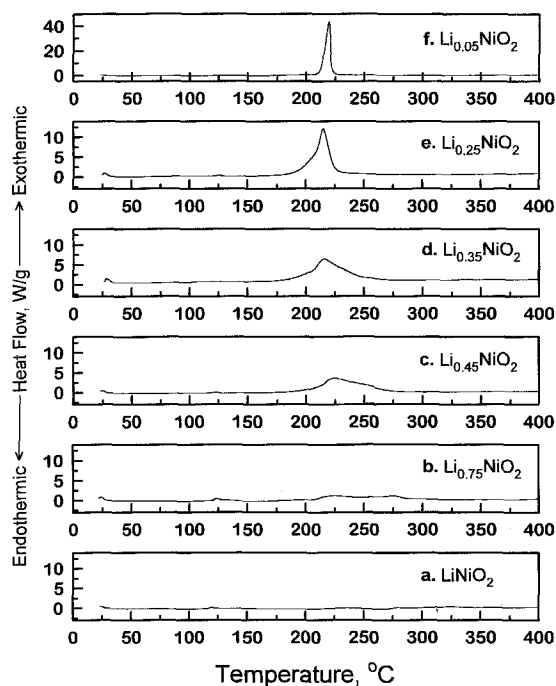


Fig. 1. DSC curves for Li_xNiO_2 plus electrolyte.

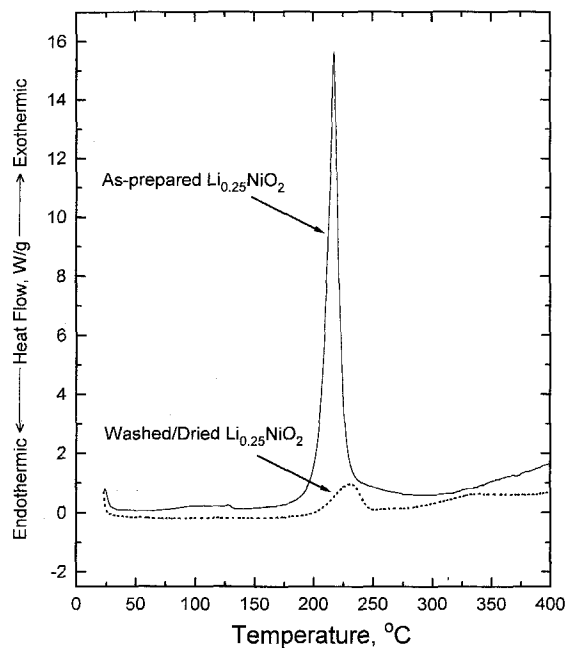


Fig. 2. DSC curves comparing $\text{Li}_{0.25}\text{NiO}_2$ with and without a washing/vacuum-drying procedure to remove electrolyte.

EC/DMC solvent mixture was reintroduced to dried samples, the reactivity returned, but at a somewhat lower level, suggesting that both the solvents and the salt were involved in the reactions. Further work will be necessary to quantify their relative contributions.

Fig. 3 shows the results of similar experiments with Li_xCoO_2 plus electrolyte. The onset temperature of the

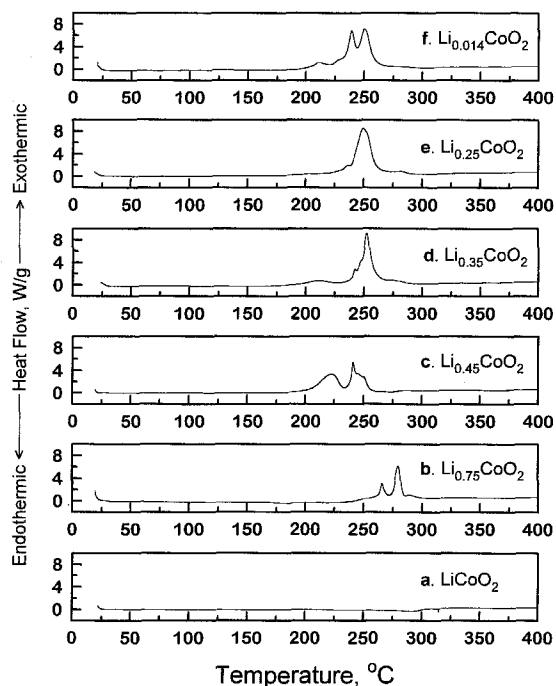


Fig. 3. DSC curves for Li_xCoO_2 plus electrolyte.

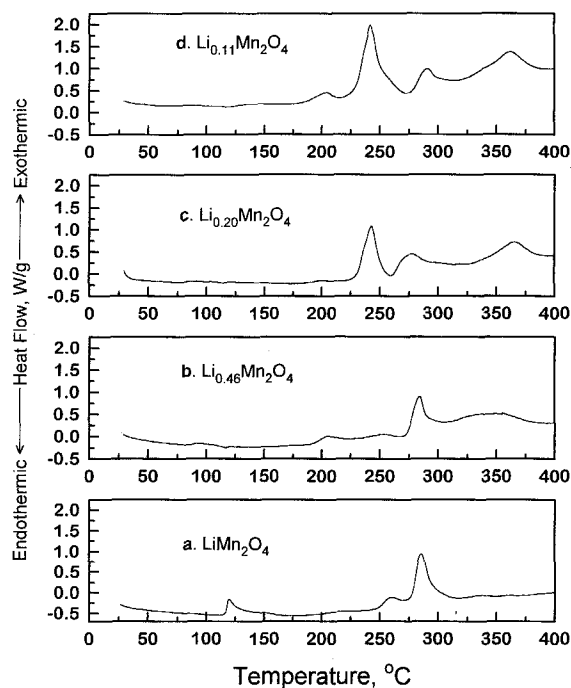


Fig. 4. DSC curves for $\text{Li}_x\text{Mn}_2\text{O}_4$ plus electrolyte.

major exothermic peak was about 230 °C, slightly higher than that of Li_xNiO_2 . Split exothermic peaks were generally observed, suggesting possible slower reaction kinetics. In general, the thermal characteristics of Li_xCoO_2 plus electrolyte were similar to Li_xNiO_2 but with somewhat lower reactivity.

Fig. 4 shows similar DSC curves for $\text{Li}_x\text{Mn}_2\text{O}_4$ plus electrolyte. LiMn_2O_4 exhibited some reaction with the electrolyte starting at about 250 °C. Two peaks between 250 and 300 °C were observed. For $\text{Li}_{0.2}\text{Mn}_2\text{O}_4$, the onset temperature shifted to a lower temperature of 225 °C and an additional peak starting at 325 °C was also observed.

The overall heat generation under the exothermic peaks is a direct indication of the reactivity between the active materials and the electrolyte. Fig. 5 summarizes the data as a function of charge capacity. It shows that highly delithiated Li_xNiO_2 was the most reactive material. Li_xCoO_2 was slightly less reactive than Li_xNiO_2 , while the reactivity of $\text{Li}_x\text{Mn}_2\text{O}_4$ was the lowest and the least sensitive to changes in x . The nearly linear increase in reaction energy as a function of the charging states of the oxide materials suggests that the reaction amplitude depends on the available M^{4+} , particularly where $\text{M} = \text{Ni}$ or Co , and that Mn^{4+} exhibits less oxidation capability relative to the others. Although Li_xNiO_2 and Li_xCoO_2 can be charged to low x values and produce high cell capacities, the results here suggest that this will result in a significant penalty in overall cell safety.

Fig. 6 shows typical DSC curves for MCMB25-28 carbon plus electrolyte. The unintercalated sample showed

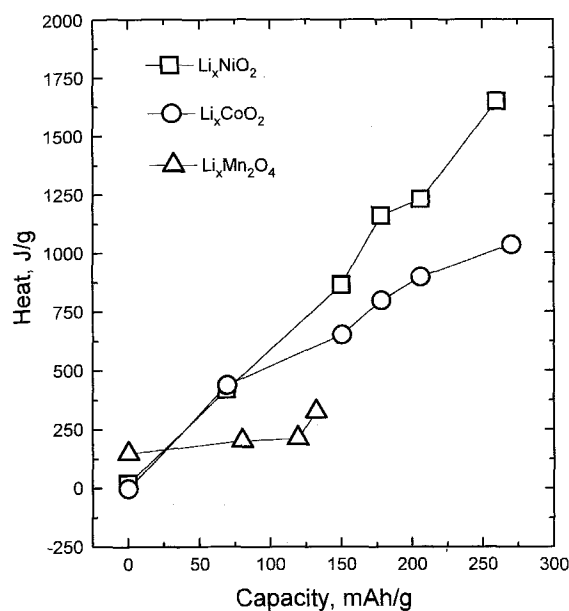


Fig. 5. Overall heat generation of the three lithium transition metal oxides as a function of charge capacity.

only the electrolyte endothermic peak at about 270 °C, which was also observed for LiNiO_2 and LiCoO_2 . After charging to a capacity of 85 mAh/g ($\text{Li}_{0.23}\text{C}_6$), 170 mAh/g ($\text{Li}_{0.46}\text{C}_6$) and 340 mAh/g ($\text{Li}_{0.91}\text{C}_6$), all these intercalated samples exhibited a small exothermic reaction with a low onset temperature of about 130 °C. However, the heat associated with these peaks was small (44, 26 and 41 J/g, respectively, for this series), and independent of the x values in Li_xC_6 . Over many experiments, the maxi-

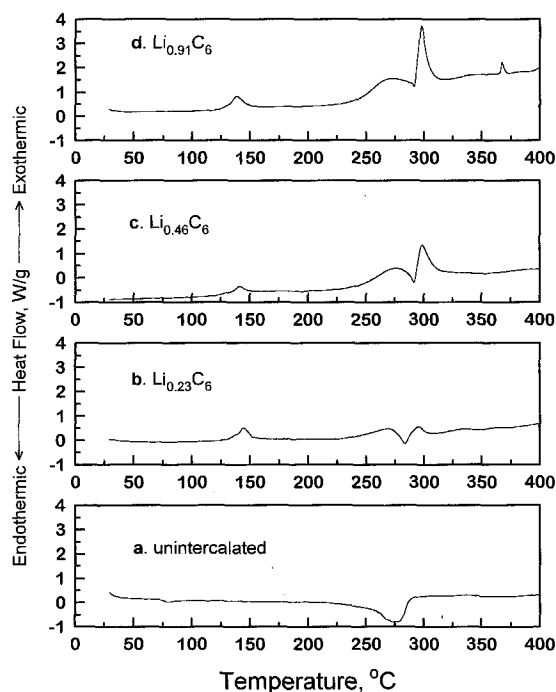


Fig. 6. DSC curves for Li_xC_6 plus electrolyte.

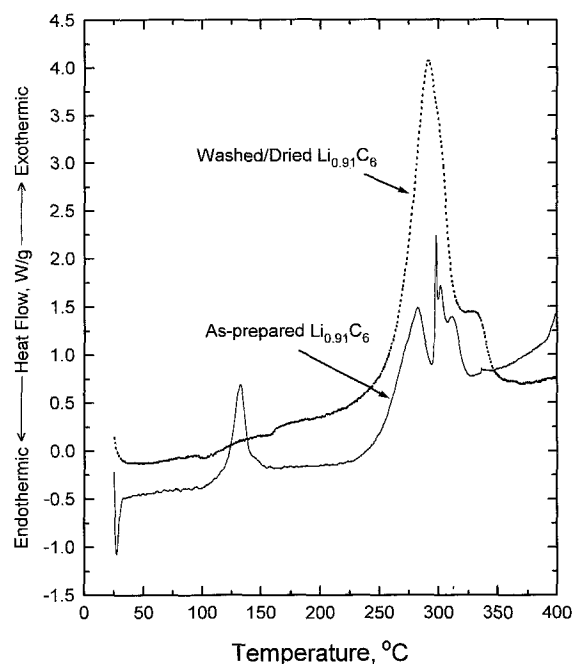


Fig. 7. DSC curves comparing $\text{Li}_{0.91}\text{C}_6$ with and without a washing/vacuum-drying procedure to remove electrolyte.

imum value observed was 120 J/g. The data suggest that these peaks were therefore related to the surface passivation of the lithiated carbon materials. With all the Li-intercalated samples, a second broad peak was observed starting at 230 °C and the reaction heat increased as x increased. This peak appeared to be superimposed with the electrolyte endothermic peak and, thus, the resulting net heat generation was not very high. For example, the integrated heat for the fully intercalated sample $\text{Li}_{0.91}\text{C}_6$ was about 360 J/g compared with a maximum of 1600 J/g for the Li_xNiO_2 samples. The exothermic peaks for the carbon samples were also broader, spanning a 100 °C range (a 10 min interval). This relatively slow reaction might be related to slow diffusion of Li out of the MCMB25-28 lattice.

Fig. 7 compares $\text{Li}_{0.91}\text{C}_6$ with and without the washing/vacuum-drying procedure. The peak at 130 °C disappeared after the washing/vacuum-drying procedure (and came back after reintroducing electrolyte), but the higher temperature peak remained and increased somewhat in magnitude. The increase may have been due to the absence of the electrolyte endothermic decomposition and evaporation. Very recent DSC data have indicated that the high temperature peak may be the result of reactions between the PVDF binder and Li.

4. Conclusions

DSC has proven to be a useful technique to study the reactivity of active materials used in Li-ion cells. The

present study indicated significant exothermic reaction between commonly used cathode materials and electrolytes. The reactions appeared to be due to contributions from the solvents, and possibly the salt. Both Li_xNiO_2 and Li_xCoO_2 exhibited strong reactivity with onset temperatures in the 200 to 230 °C range as x was decreased, suggesting that control of the stoichiometry of these materials is very important for achieving system safety. In contrast, $\text{Li}_x\text{Mn}_2\text{O}_4$ reaction occurred at about 225 °C with less energy and less sensitivity to changes in x . Li-intercalated carbon in the presence of electrolyte produced DSC exotherms in two temperature ranges. The first was a low energy peak with onset temperature at approximately 130 °C, which appeared to be due to surface passivation of the lithiated carbon materials. The second peak started at about 230 °C and may have involved the PVDF binder material of the electrodes. Further work is underway to determine the mechanisms responsible for the exothermic reactions for both the cathode and the anode materials. Data of this nature are invaluable in the design of safe, high energy density electrochemical systems.

Acknowledgements

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