Thermal Instability of Olivine-Type $LiMnPO_4$ Cathodes

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Abstract

The remarkable thermal stability of $LiFePO_4$ and its charged counterpart, $FePO_4$, have been instrumental in its commercialization as a lithium ion battery cathode material. Despite the similarity in composition and structure, and despite the high thermal stability of the parent compound, $LiMnPO_4$, we find that the delithiated phase Li_yMnPO_4, (which contains a small amount of residual lithium), is relatively unstable and reactive toward a lithium ion electrolyte. The onset temperature for heat evolution in the presence of 1M $LiPF_6$ in 1:1 ethylene carbonate/propylene carbonate is around 150 °C, and the total evolved heat is 884 J/g, comparable to that produced under similar conditions by charged $LiCoO_2$ electrodes.

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1. Introduction

It is well known that charged oxide cathodes such as Li_xCoO_2, Li_xNiO_2, $Li_xMn_2O_4$, $Li_xNi_{0.8}Co_{0.2}O_2$, $Li_x(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$, and $Li_y[Ni_xCo_{1-2x}Mn_x]O_2$ decompose and release O_2 at elevated temperatures. [1-5] The released O_2 can ignite the organic solvents in the electrolyte and create hazardous conditions including fire and explosion. Olivine-type $LiMPO_4$ (M = Fe, Mn, Co and Ni) compounds have been promoted as safe alternatives. The strong covalent P-O bonds in the tetrahedral $(PO_4)^{3-}$ anion are believed to inhibit oxygen loss. Heterosite $FePO_4$ is stable in air up to 600 °C, above which it transforms into quartz-like $FePO_4$ without losing oxygen. [6] When $FePO_4$ is mixed with $LiFePO_4$, the miscibility gap between the two end members shrinks and single-phase solid solutions are formed at temperatures above 250 °C. [7-9]

Our recent study, [10] however, revealed that fundamental differences exist between $LiFePO_4$ and $LiMnPO_4$. Chemical or electrochemical delithiation of sub-micron sized crystals of $LiMnPO_4$ at room temperature produced nonstoichiometric Li_yMnPO_4 phases with $y < 0.16$. When $x LiMnPO_4/(1-x)Li_yMnPO_4$ ($0 \le x < 1$) mixtures were heated under flowing N_2, the delithiated phase decomposed to form $Mn_2P_2O_7$ and release O_2. High temperature single-phase Li_xMnPO_4 solid solutions were not formed from the mixtures due to the instability of Li_yMnPO_4. Thermal decomposition of delithiated $LiMnPO_4$ and $LiCoPO_4$ phases have also been reported by Kim et al. [11] and by Bramnik et al [12]. Oxygen loss from these Olivines was observed at temperatures close to 200 °C.

Here we compare the thermal behavior of $LiFePO_4/FePO_4$ and $LiMnPO_4/Li_yMnPO_4$ samples using X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Heat generation in the presence of a

lithium-ion battery electrolyte is also evaluated, and its impact on the safety of high energy phosphate Li-ion batteries is discussed.

2. Experimental

2.1. Synthesis

$LiFePO_4$ and $LiMnPO_4$ crystals were synthesized using the hydrothermal method described previously. [13] $LiFePO_4$ was delithiated by treatment with a solution of bromine in acetonitrile. Chemical delithiation of $LiMnPO_4$ was achieved by stirring the crystals in a 0.1 M solution of nitronium tetrafluoroborate (NO_2BF_4, 95+%, Aldrich) in acetonitrile for 24 h, with a phosphate: oxidant mole ratio of 1:2. The reactions were carried out at room temperature in an argon-filled glovebox with $O_2 < 1$ ppm and $H_2O < 2$ ppm. Samples for *ex situ* X-ray diffraction (XRD) measurements were heated to 400 °C at a rate of 5 °C/min and held at 400 °C for 2 h in a tube furnace purged with flowing N_2 .

2.2. Characterization

X-ray diffraction patterns were acquired using a Panalytical Xpert Pro diffractometer with monochromatized Cu Kα radiation. The scan rate was 0.0025°/s in 0.01° steps. Thermogravimetric analysis (TGA) was carried out on a simultaneous thermal analyzer (STA 449 F3, NETZSCH) under flowing high-purity argon. 10-20 mg samples were loaded into covered Al_2O_3 pans in the glovebox. Data were collected between 30-600 °C with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed using a DSC 7 instrument (Perkin-Elmer). These samples were loaded into hermetically sealed 30 µl stainless steel capsules in the glovebox and tested

from 30 to 400 °C at a 10 °C/min heating rate. The gold-gasketted capsules can withstand an internal pressure up to 150 atmospheres, which suppresses the volatilization of solvent and ensures no weight loss during the experiment. The sample size for the solid was typically between 4.5-7 mg, and the solid to electrolyte ratio was fixed at 2:1 (w/w) to ensure the presence of excess electrolyte during the experiment. 1M $LiPF_6$ in propylene carbonate (PC) and ethylene carbonate (EC, Ferro Corporation, 50:50 by volume and 44:56 by mole ratio) was used as electrolyte in this study.

3. Results and Discussion

The hydrothermal $LiFePO_4$ crystals measuring 2 μm x 0.2 μm x 4 μm and $LiMnPO_4$ crystals measuring 0.4 μm x 0.1 x 0.6 μm along the *a*, *b*, and *c*-axes were uniform hexagonal plates with low specific surface area (< 1 m^2/g), comparable to samples prepared by solid-state synthesis. When the phosphate crystals were heated to 400 °C under flowing N_2, no structural change was observed by XRD. Delithiated $LiFePO_4$ crystals were also found to be stable during the thermal treatment, consistent with previous reports.

When a chemically delithiated, single phase Li_yMnPO_4 sample (with *y* close to 0) was heated under the same conditions, structural decomposition occurred. Fig. 1 compares the XRD pattern of the phase before and after the thermal treatment. All of the new peaks on the pattern from the heated sample can be indexed based on $Mn_2P_2O_7$, with the strongest diffraction peaks located at 29° and 30.5°. The decomposition reaction releases O_2 according to Equation 1, with a theoretical weight loss of 5.4%.

$$2MnPO_4 \rightarrow Mn_2P_2O_7 + 0.5O_2 \qquad [1]$$

The TGA profiles for phosphate samples are shown in Fig. 2. The delithiated Li_yMnPO_4 sample started to lose weight around 120 °C and had a total weight loss of 7% at 400 °C, higher than the theoretical value. This may due to absorption moisture from the air during transfer to the instrument, as the delithiated phase is known to be highly hydroscopic. In addition to its own contribution to weight loss, water can cause volatilization of phosphoric acid. It is also possible that some $Mn_2P_2O_7$ decomposes further, with additional oxygen loss. $LiMnPO_4$, $LiFePO_4$ and $FePO_4$ all maintained constant weight throughout the experiments, consistent with the XRD results.

Heat evolution during the thermal decomposition of the phosphates was evaluated by differential scanning calorimetry. The pure electrolyte, 1M $LiPF_6$ in EC and PC, had an exothermic peak centered at 325 °C, as shown in Fig. 3a. The total amount of heat generated was 280 J/g, comparable to the value reported by Katayama et al.[14] The peak position, however, is about 30 °C higher in our DSC profile, which could be due to improved sealing of our DSC pans. The exotherm is attributed to redox reactions of $LiPF_6$ and its decomposition products, such as PF_5, with the carbonate solvents. [15]

DSC profiles of $LiMnPO_4$ and $LiFePO_4$ in the presence of the electrolyte are shown in Fig. 3b. A broad peak centered at 299 °C and a sharp peak at 294 °C were observed for $LiFePO_4$ and $LiMnPO_4$, respectively. The heat evolved was 157 J/g for $LiFePO_4$ and 154 J/g for $LiMnPO_4$, consistent with the known low reactivity of these phases.

When chemically delithiated $FePO_4$ alone was heated to 400 °C, no heat signal was detected (Fig. 3c). Three exothermic peaks, centered at 173, 250 and 329 °C, were observed for Li_yMnPO_4 (the sharp peak at 280 °C is an artifact). The total heat generated

was 200 J/g, corresponding to the exothermic reaction that releases O_2. This is consistent with the TGA results, confirming that Li_yMnPO_4 decomposes above 120 °C while $FePO_4$ is stable.

The heat generated increased significantly when electrolyte was present with the delithiated phosphates (Fig. 3d). A series of overlapping peaks with onset temperatures of 250 °C and centered at 270, 280 and 315 °C were observed for $FePO_4$, accounting for a total heat of 204 J/g. For Li_yMnPO_4, three main peaks were observed. The first ranged from 150 to 210 °C and was centered at 175 °C, with a total heat of 103 J/g. The second and third peaks overlapped, with onset at 215 °C, peak centers at 256 and 300 °C, and total heat of 781 J/g.

When electrolyte is present, the solvents can be oxidized by oxygen released from the electrode material. The heats of combustion[16] of PC and EC are 1818 kJ/mol and 1161 kJ/mol, and require 4 and 2.5 mol of O_2 respectively according to Equations [2] and [3]:

$$\text{PC:} \quad C_4H_6O_3 + 4O_2 \rightarrow 4CO_2 + 3H_2O \qquad [2]$$

$$\text{EC:} \quad C_3H_4O_3 + 2.5O_2 \rightarrow 3CO_2 + 2H_2O \qquad [3]$$

This corresponds to 455 kJ/mol of O_2 for PC and 464 kJ/mol of O_2 for EC. For a PC: EC mole ratio of 44:56, and the release of 0.25 mol of O_2 per mole of $MnPO_4$, the total heat generated is calculated to be 768 J per g of $MnPO_4$, assuming all the released O_2 was consumed in solvent combustion. This is in good agreement with the measured value of 781 J/g.

Thermal runaway of Li-ion batteries occurs when the heat output exceeds thermal dissipation of the system. Exothermic reactions between the electrolyte and the cathode

materials at elevated temperatures are considered to be primary contributors to thermal runaway. Lithium-ion cells, therefore, must pass a number of safety tests before they can be shipped and marketed.[17-18] Since the outcome of the thermal tests (pass or fail) is typically determined by the activity below 250 °C, [19] the reaction heat released within this range is considered as one of the most important safety indicator of the cathode. Other factors, such as the onset and peak temperatures of the exothermic reactions, are also considered.

The thermal behaviors of current and potential cathodes for Li-ion batteries in contact with electrolytes have been studied extensively by DSC, accelerating rate calorimetry (ARC), and microcalorimetry. For comparison, we consider data that were collected from samples with similar surface areas and that were studied by DSC or microcalorimetry. Table 1 compares the amount of heat released by various charged cathode materials that are currently of commercial interest. For electrochemically delithiated oxide electrodes, thermal reactivity is largely dependent on the end-of-charge voltage. For consistency, the literature data in Table 1 are from electrodes that were charged to 4.2 V. $LiNiO_2$ is known for its thermal instability, as it releases 1600 J/g (highest among those tested) with an onset at 184 °C and peak center at 214 °C.[20] To improve its thermal behavior, other metals such as Co, Al and Mn have been used to replace a certain percentage of the Ni. These substituted electrodes, such as $LiNi_{0.8}Co_{0.2}O_2$, $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$, and $Li(Ni_xCo_{1-2x}Mn_x)O_2$, have been found to have much greater thermal stabilities. [20-22] The most stable variation, $Li(Ni_xCo_{1-2x}Mn_x)O_2$ (x=1/4), releases only 178 J/g at 285 °C, about one tenth of that released by $LiNiO_2$. $LiCoO_2$ and $LiMn_2O_4$ were reported to release 760 J/g at 231 °C and 990 J/g 289 °C,

respectively. Although the total heat is higher for $LiMn_2O_4$, it is considered a safer material because the majority of the heat is released above 250 °C.

$LiFePO_4$ is the safest cathode among those tested. The charged material has a high onset temperature of 250 °C and peak exotherm at 280 and 315 °C on the DSC profile. The amount of heat released is only 147 J/g, according to Yamada et al. [23] Xiang et al [4] and Joachin et al, [24] reported 260 J/g at 268 °C and 145 J/g at 277 °C, respectively. These results are in good agreement with our study where $FePO_4$ was found to release 204 J/g of heat peaked at 270, 280 and 315 °C.

Three exothermic peaks were observed in the DSC profile of Li_yMnPO_4. The first peak (150 to 210 °C) is likely due to the release of O_2 from the phosphate. The combustion of the carbonate solvents then begins at 215 °C, the onset temperature of the second exothermic peak. The total heat generated was 884 J/g, with the peak at 256 °C. This is comparable to the results for $LiCoO_2$, $LiNi_{0.8}Co_{0.2}O_2$ and $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$. Surprisingly, the phosphate, is more reactive than $LiMn_2O_4$ and the Mn-substituted oxides, $Li(Ni_xCo_{1-2x}Mn_x)O_2$.

Although $LiFePO_4$ is an intrinsically safe Li-ion cathode, $LiMnPO_4$ does not appear to have a safety advantage over the oxides. While the PO_4 group in the olivine structure has been credited with conferring higher voltages and increased stability on phosphate cathodes, this work demonstrates the large influence of the transition metal on both kinetics and thermodynamics of these materials. Upon oxidation of $LiMnPO_4$, the presence of the Jahn-Teller ion (Mn^{3+}) causes structure instability due to the difficulty in lattice distortion. The accumulated strain energy restricts the growth of the delithiated $LiMnPO_4$ domains, which further decreases phase stability due to the high amount of

reactive surface area in small domains. Moreover, manganese may also have a catalytic effect on the decomposition of the phosphate to release oxygen. The thermal instability of $LiMnPO_4$ may prove to be a barrier to its use in high energy lithium-ion batters, especially for vehicle applications where safety is of paramount importance.

Finally we wish to emphasize that the rate of heat release during thermal decomposition is directly related to the particle size and the specific surface area of the active material. [25] Nanosized $LiMnPO_4$ samples that are currently being investigated can be expected to generate heat at lower temperatures, and may react more completely. In a recent DSC study by Martha et al, [26] heat evolution of both lithiated and delithiated 25-30 nm $LiMnPO_4$ particles was compared to that for $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ in a 1M $LiPF_6$ in EC and DMC (1:1) electrolyte. Upon heating to 300 °C, the delithiated $LiMnPO_4$ had a total heat evolution of 954 J/g with a peak onset of 194 °C and centered at 220 °C, which showed it to be more reactive than our larger crystals. The authors, however, concluded that their carbon-coated $LiMnPO_4$ was safer compared with the oxide, as the heat evolution was only half of that released from a delithiated $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ electrode (1863 J/g). Curiously, however, the uncharged electrode released even more heat (2068 J/g) than its delithiated counterpart.

4. Conclusions

In the presence of a Li-ion battery electrolyte, delithiated $LiMnPO_4$ exhibited strong exotherms consistent with combustion reactions with the electrolyte solvents. The total released heat of 884 J/g beginning at 150 °C and peaking at 256 °C was comparable to that exhibited by charged $LiCoO_2$ electrodes. While $LiFePO_4$ has good thermal

characteristics and has been shown to be a safer cathode, $LiMnPO_4$ does not appear to have the same advantage. This instability must be addressed before this cathode material can be commercialized.

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Figure captions

1. X-ray diffraction patterns of the Li_yMnPO_4 sample before and after thermal treatment.
2. TGA curves for $LiFePO_4$, $LiMnPO_4$, $FePO_4$ and Li_yMnPO_4
3. DSC comparison of: a) 1M $LiPF_6$ in EC/PC; b) $LiFePO_4$ and $LiMnPO_4$ with the electrolyte; c) $FePO_4$ and Li_yMnPO_4; d) $FePO_4$ and Li_yMnPO_4 with the electrolyte

Table 1. Heat generation from charged cathodes

Material	Onset temperature (°C)	Peak temperature (°C)	Electrolyte *	Evolved Heat (J/g)
$LiNiO_2$ [20]	184	214	EC/DEC (33/67)	1600
$LiCoO_2$ [20]	180	231	EC/DEC (33/67)	760
$LiMn_2O_4$ [20]	207	289	EC/DEC (33/67)	990
$LiNi_{0.8}Co_{0.2}O_2$ [20]	193	213	EC/DEC (33/67)	1200
$Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ [21]	220	253/268	EC/EMC (30/70)	980
$Li(Ni_xCo_{1-2x}Mn_x)O_2$ [20] x=3/8	270	297	EC/DEC (33/67)	290
$Li(Ni_xCo_{1-2x}Mn_x)O_2$ [22] x=1/4	280	285	EC/DEC (33/67)	178
$LiFePO_4$ [23]	250	280/315	PC/DMC	147
$LiMnPO_4$ **	150/215	175/256/300	EC/PC (50/50)	103/781

* The electrolyte salt is 1M $LiPF_6$ except in reference 21 where 1.2M $LiPF_6$ was used.

** This work

Figure 1

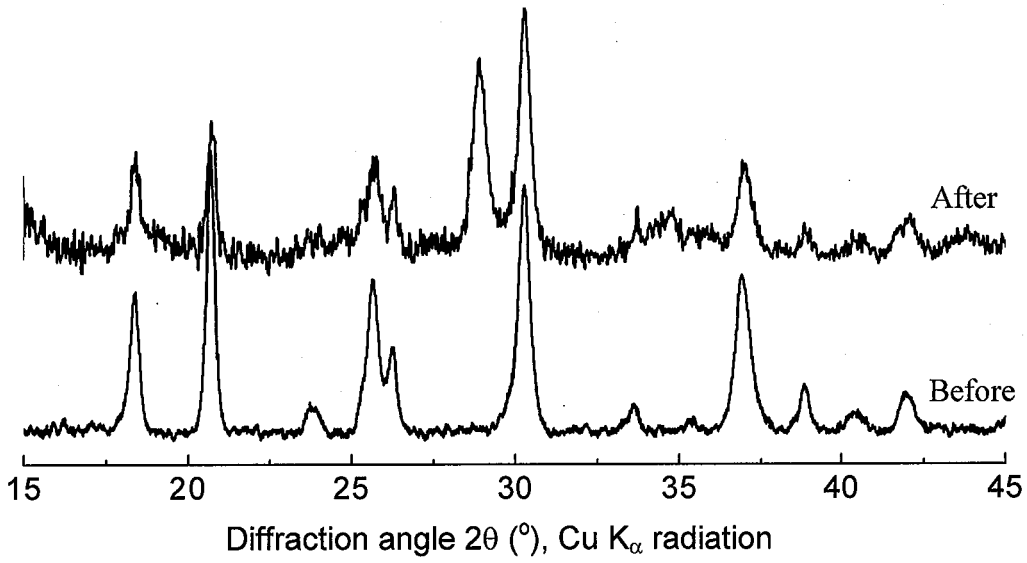

After
Before
15
20
25
30
35
40
45
Diffraction angle 2θ (°), Cu Kα radiation

Figure 2

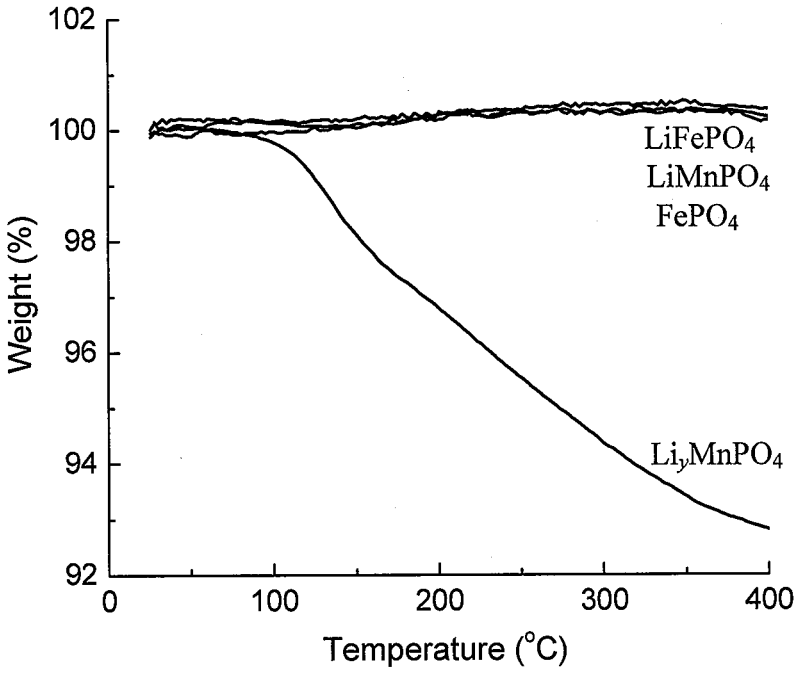
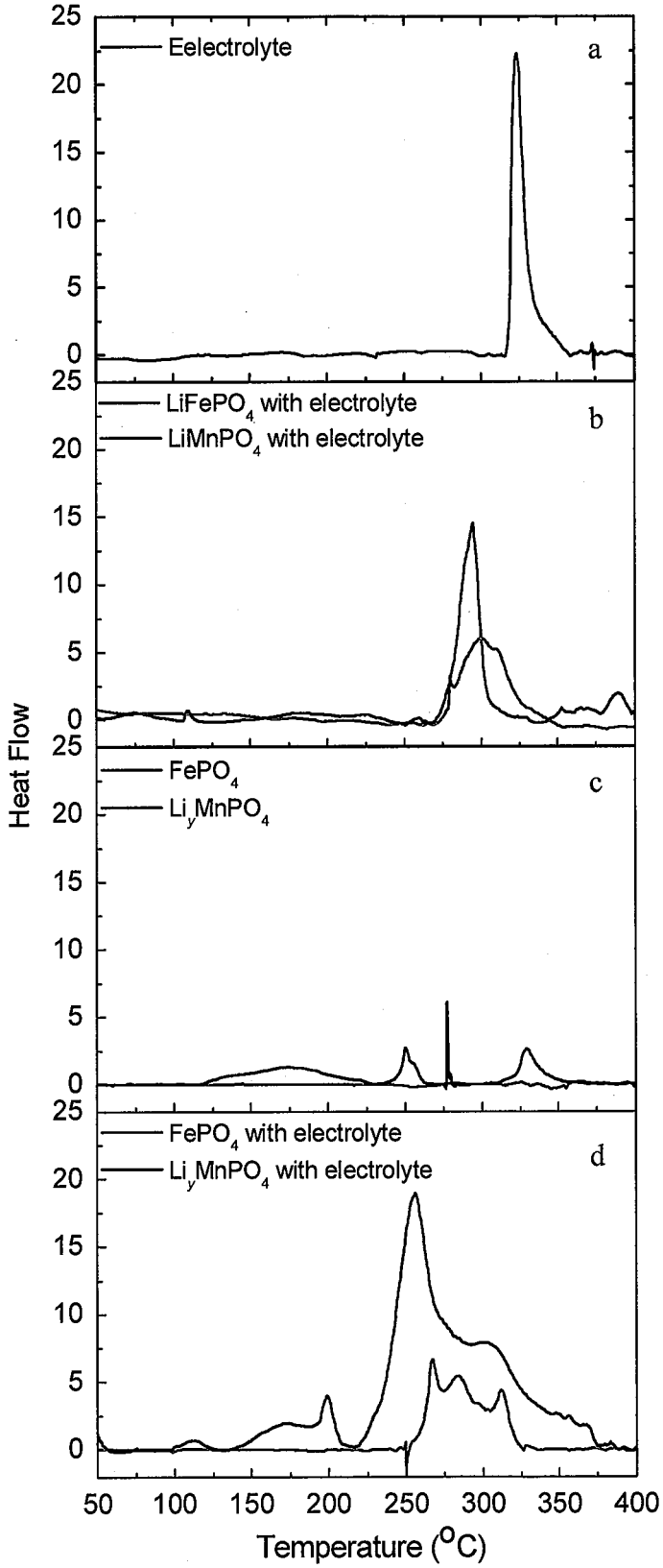

102
100
98
96
94
92
Weight (%)
0
100
200
300
400
Temperature (°C)
LiFePO4
LiMnPO4
FePO4
LiyMnPO4

Figure 3


Eelectrolyte
a
LiFePO4 with electrolyte
LiMnPO4 with electrolyte
b
FePO4
LiyMnPO4
c
FePO4 with electrolyte
LiyMnPO4 with electrolyte
d
Heat Flow
Temperature (°C)
25
20
15
10
5
0
50
100
150
200
250
300
350
400