

Articles

Thermal Behavior of Li_xCoO_2 Cathode and Disruption of Solid Electrolyte Interphase Film

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Received May 2, 2008, Accepted September 30, 2008

Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and ion chromatography (IC) were employed to analyze the thermal behavior of Li_xCoO_2 cathode material of lithium ion battery. The mass loss peaks appearing between 60 and 125 °C in TGA and the exothermic peaks with 4.9 and 7.0 J/g in DSC around 75 and 85 °C for the Li_xCoO_2 cathodes of 4.20 and 4.35 V cells are explained based on disruption of solid electrolyte interphase (SEI) film. Low temperature induced HF formation through weak interaction between organic electrolyte and LiF is supposed to cause carbonate film disruption reaction, $\text{Li}_2\text{CO}_3 + 2\text{HF} \rightarrow 2\text{LiF} + \text{CO}_2 + \text{H}_2\text{O}$. The different spectral DSC/TGA pattern for the cathode of 4.5 V cell has also been explained. Presence of ionic carbonate in the cathode has been identified by ion chromatography and LiF reported by early researchers has been used for explaining the film SEI disruption process. The absence of mass loss peak for the cathode washed with dimethyl carbonate (DMC) implies ionic nature of the film. The thermal behavior above 150 °C has also been analyzed and presented.

Key Words: Cathode, Li_xCoO_2 , Thermal analysis, Thermal stability, Solid electrolyte film

Introduction

During the recent past much emphasis has been placed over the safety aspects of lithium ion batteries following the reports of battery explosions in note book computers and cell phones.¹ Such untoward incidents call for thermal studies to unravel the cause for battery explosion.^{2,3} Even though the lithium cells contain highly reactive electrode materials along with flammable electrolyte, under ambient temperatures the electrodes exhibit phenomenal stability owing to solid electrolyte interphase film (SEI), a protective cover formed over the electrode particles during initial charging process.⁴ This thin SEI film, reported to be an electronically resistive, allows easy diffusion of lithium ions for providing cycle life characteristics.⁵ Nevertheless, during battery abuse conditions the passage of high currents cause destruction of SEI film making direct contact of the electrolyte with the electrode materials leading to battery failure.⁶ Richard and Dahn describe that at elevated temperatures, the SEI film is not stable which is why a rechargeable Li battery with a Li metal anode is unsafe.⁷ Hitoshi Ota *et al.* analyzed the SEI layer of LiCoO_2 cathode in poly propylene carbonate based electrolyte containing ethylene sulphite additive with sulfur K-edge X-ray absorption near-edge structure spectroscopy (S K-edge XANES) and reported the presence of alkyl sulphide species on the SEI layer over LiCoO_2 particles.⁸ X-ray photoelectron spectroscopy reveals that the SEI films form only over LiCoO_2 particles but not on the binder.⁹

Through XPS studies reported the cell charged to higher

voltage has greater amount of LiF deposition and suggested the formation of HF, an environment from the release of proton by organic solvent.¹⁰ Many authors have carried out thermal studies of cathodes washed with DMC in the presence of organic electrolyte solvents.^{11,12}

This paper describes the thermal behavior of Li_xCoO_2 cathode material with an emphasis on low temperature thermal behavior of the cathode material around 100 °C. Further, this investigation is unique in the sense that it reports for the first time a new peak attributed possibly to temperature induced solid electrolyte interphase film break down at low temperature region of the Li_xCoO_2 cathode.

Experimental

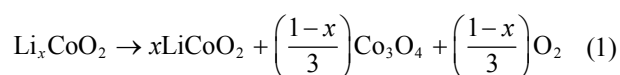
Pouch cells with 1000 mAh capacity of dimensions 60 mm × 33 mm × 4 mm received from a manufacturing company is used for this experiment. The data provided by the company reveals that the cathode constituents are LiCoO_2 , Super "P" Battery black (WILLEBROEK, Belgium) and polyvinylidene difluoride (Aldrich) coated over an aluminum current-collector in the weight ratio 94:3:3, respectively. The particle size of Li_xCoO_2 is 20 μm. The anode material constituents coated over a copper current-collector comprises a blend made up of mesocarbon microbeads and polyvinylidene difluoride (PVDF) in the weight ratio 92:8. The electrolyte is 1.12 M LiPF_6 with 2 wt% vinylene carbonate (VC) dissolved in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed in 1:1(v/v) ratio. The cell was first preconditioned by cycling

three times between 2.5 and 4.2 V and stabilized at OCV = 3.85, 3.95, 4.20, 4.35 and 4.5 V by constant potential charging using Toyo Instrument (TOSCAT 3100). The cells charged to different voltages were carefully opened and the cathode material was removed from the aluminum foil current collector. The collected material was stored in a bottle for carrying out TGA (TGA-Q600, TA Instrument USA) and DSC (DSC-Q1000) analysis. Both instruments use data processing program with universal analysis, 2000.

Sample material washed in dimethyl carbonate solvent (DMC) was considered for thermogravimetric analysis to assess the nature of the film formed over the cathode. The electrode cut in size 20 mm × 10 mm was kept immersed in 50 mL of distilled water for 1 h and the solution was used to identify the presence of carbonate ions present in the cathode using ion chromatography (IC). The material preparation was carried out in a dry-room maintained at ~21 °C with dew point temperature ~-65 °C.

Results and Discussion

Thermal behavior of the cathode. The TGA along with derivative profiles for electrodes charged to different voltages are presented as Fig. 1 and Fig. 2. The figures show the weight loss occurs in three different regions. The weight loss in the region around 100 °C may be due to solvent evaporation and between 200 and 400 °C the decomposition of Li_xCoO_2 into LiCoO_2 , Co_3O_4 and oxygen. The formation of lower valent cobalt compound could also be expected at higher temperature depending on the availability of carbonaceous materials which could have come through the decomposition of electrolyte solvent and PVDF (melting point 165 °C) as well from the participation of conductive carbon present in the sample.^{6,7} Above 170 °C carbonaceous material assisted Li_xCoO_2 decomposition proceeds, at still higher temperature the decomposition leads to lower valent cobalt compounds.¹¹ The figure from TGA shows that only highly charged electrode materials such as 4.20, 4.35, and 4.5 V undergo much weight loss. The lower weight loss in 4.5 V cathode may be attributed to the decomposition of the cathode and electrolyte in the cell itself due to 4.5 V charging. The thermal decomposition of Li_xCoO_2 in the region above 125 °C may be represented by the equation



It is also reported that the overcharged Li_xCoO_2 cathode remains in highly de-lithiated state. But as $x \rightarrow 0$ the cathode becomes more unstable and any destabilizing factors such as increase of temperature could lead to the formation of LiCoO_2 , Co_3O_4 and O_2 which follows an exponential relationship with temperature.^{13,14}

Nature of the SEI film. Fig. 3 illustrates the TGA and its derivative curves for the washed and unwashed cathode samples of the cells charged to 4.35 V. The profile shows absence of mass loss for the sample washed with DMC in the region around 100 °C suggesting that the solvent DMC has removed the constituents/materials responsible for the appearance of mass loss peaks appeared for the pristine sample. The solvent DMC with low dielectric constant (ϵ) ~3 could serve to remove the electrolyte as well any ionic materials present in the cathode materials.^{11,12} The low temperature peak appeared is whether due to the evaporation of the organic solvent or through any other oxidation reaction could be understood from the DSC spectrum.

Differential Scanning calorimetry. As DSC explains the exact nature of mass loss on the cathodes of 3.85, 3.95, 4.20, 4.35, and 4.5 V cells, the experimental results obtained using

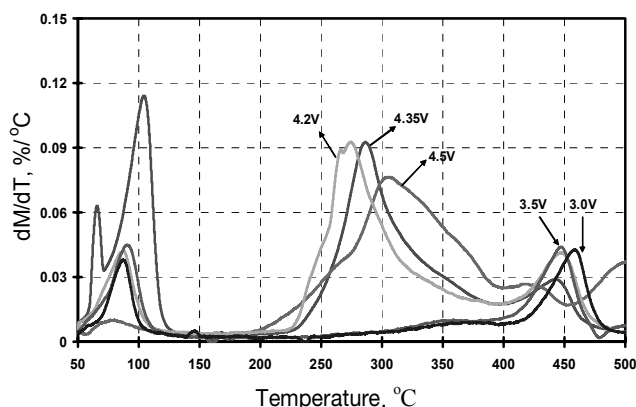


Figure 2. dM/dT (%/°C) as a function of temperature (°C) for cathode material of cells charged to 3.85, 3.95, 4.20, 4.35 and 4.5 V.

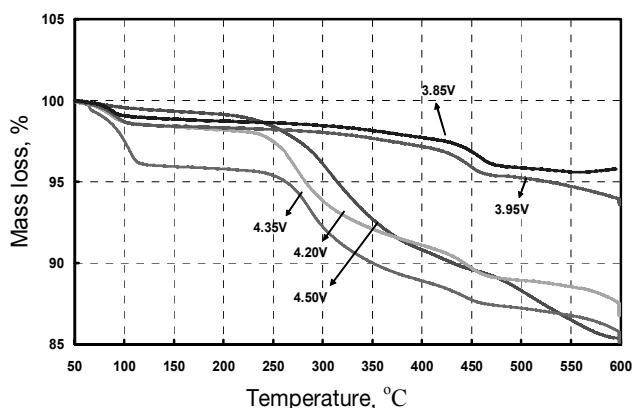


Figure 1. TGA curves for cathode material of cells charged to 3.85, 3.95, 4.20, 4.35 and 4.5 V.

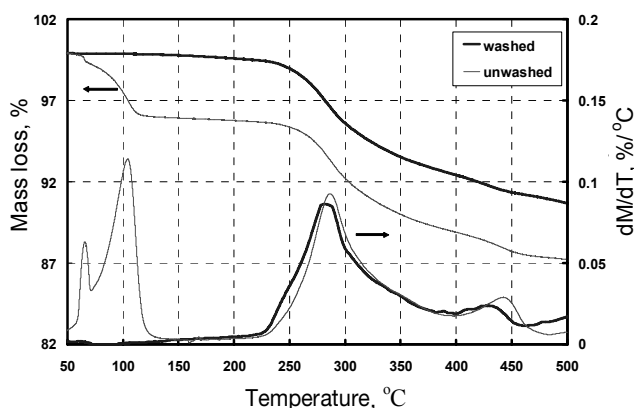


Figure 3. TGA patterns of washed and unwashed Li_xCoO_2 cathode of 4.35 V cell.

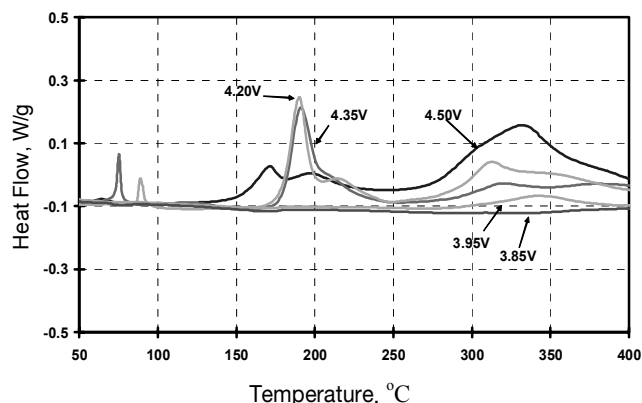


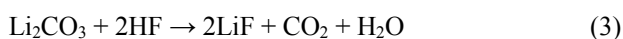
Figure 4. DSC scans for the cathodes of 3.85, 3.95, 4.20, 4.35 and 4.5 V cells.

DSC are presented in Fig. 4. The figure shows that the cathodes of cells charged to 3.85 and 3.95 V have no peaks in the low temperature region whereas the cells charged to 4.20 and 4.35 V have well defined peaks of the order of 4.9 and 7.0 J/g respectively below 100 °C. The cathode of 4.5 V does not only has poor peak below 100 °C but also possess two shoulder peaks in 150 to 225 °C region possibly due to the presence of two distinct phases formed during over charge exposure of the cathode in the cell.⁶ The curve also shows that the exothermic energy release between 125 and 250 °C are 83, 80, and 50 J/g and above 250 °C are 81, 17, and 94 J/g for the respective cathodes of 4.20, 4.35 and 4.5 V cells.

Identification of carbonate species by ion chromatography.

Earlier reports state that the charged cathode has LiF coated layers due to the decomposition of LiPF_6 .^{10,12} The amount of LiF formed becomes more when the charging potential range is kept at higher value; however no mention has been made of the presence of Li_2CO_3 in the cathode.^{9,10} Presence of carbonate in the electrodes were identified by immersing the electrode in distilled water for 1 hour using ion chromatography (IC) technique and presented as Fig. 4. The curves show the presence of ionic carbonates in the solutions. The fluoride peaks appearing in the curves would have come not only from the process occurred within the cell but also from the hydrolysis of electrolyte salt present in the electrode materials during immersion of the electrode in the distilled water.

SEI film-break down mechanism. The following two reactions may be visualized to take place consecutively around 100 °C. At first proton is released¹⁰ from the organic solvent due to the weak interaction between the cathode materials and organic solvent which then reacts with LiF leading to the formation of HF. Thus formed HF then reacts with the carbonates present in the SEI film



The reaction (3) is followed by the conversion of formed LiF into HF, thus further enhancing the acidity. This process will convert the rigid SEI layer into fragile one especially as liquid phase allowing easy diffusion of the available organic

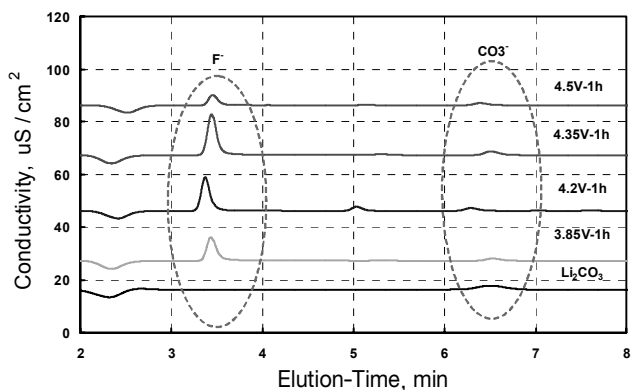


Figure 5. Identification of carbonate species in different cathodes through Ion Chromatography

solvent from the bulk into the surface of the oxide cathode. Since this oxide with x value of Li_xCoO_2 remains between 0.45 and 0.3, a large anisotropic volume change of 3% is expected to occur following phase transition and instability between hexagonal and monoclinic H1-3 phases.^{15,16} Such unstable cathode^{6,17} is expected to react with the organic solvent releasing heat energy. The foregoing results unravel the fact that the formation of HF along with high oxidation state of the cathode is could have favored the formation of exothermic peak around 100 °C. These observations can be compared with the experimental findings that only highly charged batteries release high heat energy and even could cause explosion upon battery abuses.⁶

Conclusion

This paper has discussed the general thermal process that takes place in the cathode material through the use of TGA and also discussed the new exothermic peak formed at low temperature regions through DSC experiments. The cause for the appearance of the exothermic peak is explained as due to disruption of the SEI film, thermally induced by acidic environment that shifted solid SEI phase into liquid phase favoring easy access of the organic solvent of the electrolyte to the surface of the cathode. The formation of HF along with high oxidation state of the cathode could have influenced the formation of exothermic peak around 100 °C. The extent of this initial energy release may be playing a crucial role in triggering the chain of other processes which may lead to battery explosion during battery abuse conditions.

Acknowledgments. This work has been carried out at Battery Research Group of KERI supported by Ministry of Knowledge Economy of Korea. One of the authors A. Veluchamy wishes to thank the Korean Federation of Science and Technology Societies, Korea for awarding Brain Pool Fellowship and also thanks CECRI/CSIR, India for granting leave.

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