



Short communication

Thermal analysis of Li_xCoO_2 cathode material of lithium ion battery

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ABSTRACT

Thermal behavior of Li_xCoO_2 cathode material from cells charged to different voltages has been analyzed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The mass loss appearing between 60 and 125 °C in TGA and the exothermic peaks with 4.9 and 7.0 J g⁻¹ in DSC around 75 and 85 °C for the Li_xCoO_2 cathodes of 4.20 and 4.35 V cells has been explained based on solid electrolyte interface (SEI) film-break down. The SEI film-break down for the highly charged cathode at low temperature region has been attributed to the conversion of lithium fluoride into hydrofluoric acid in concomitant with the reaction, $\text{Li}_2\text{CO}_3 + 2\text{HF} \rightarrow 2\text{LiF} + \text{CO}_2 + \text{H}_2\text{O}$. Presence of ionic carbonate in the positive electrode has been identified by ion chromatography (IC). The thermal peaks appearing in different temperature regions have been explained based on decomposition reaction of Li_xCoO_2 cathodes and the SEI film.

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1. Introduction

Under ambient temperature the electrodes exhibit phenomenal stability owing to solid electrolyte interface film (SEI), a protective cover formed over the electrode particles during initial charging process [1]. Even though this thin SEI film is reported to be an electronically resistive, allows easy diffusion of lithium ions for providing cycle life characteristics [2]. 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 which initiates active material degradation [3]. 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 [4]. Ota et al. analyzed the SEI layer of LiCoO_2 cathode in polypropylene 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 sulfide species on the SEI layer over LiCoO_2 cathode particles [5]. X-ray photoelectron spectroscopy reveals that the SEI film forms only over the LiCoO_2 particles but not on the binder [6].

Through XPS spectra of the cathode material it is also reported that the cell charged to higher voltage has greater amount of LiF deposition and suggested the formation of HF, an acidic environment from the release of proton by organic solvent [7]. The thermal behavior of the cathode has been reported for the cathode materials in the presence of organic electrolyte solvents especially for the cathode materials washed with DMC [8,9].

The very purpose of this paper is to present and explain the new peak appeared in the DSC curve of highly charged cathode which has not been reported so far. The exothermic reaction of the electrode materials at different temperature regions in the DSC has been analyzed giving much emphasis to the exothermic peak at lower temperature region which is assumed to be due to SEI film break down. A mechanism for the SEI film break down is proposed based on available literature and experimental data.

2. Experimental

Pouch cells with 1000 mAh capacity of dimensions 60 mm × 33 mm × 4 mm was received from a manufacturing company which uses graphite anode and lithium cobaltate cathode. The data provided by the company reveal that the cathode constituents are LiCoO_2 , Super P black (SPB) and polyvinylidene difluoride (PVDF) coated over an aluminum current-collector in the weight ratio of 94, 3, and 3%, respectively. The particle size of LiCoO_2 is 20 μm. The anode material constituents were coated over a copper

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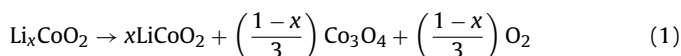
current-collector and comprised a blend made up of mesocarbon microbeads and PVDF in a weight ratio of 92 and 8%. The electrolyte (Techno Semichem.) is 1.12 M LiPF_6 with 2 wt.% vinylene carbonate (VC) dissolved in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed in 1:1(v/v) ratio. The 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, and 4.35 by constant potential charging. The cells charged to different voltages were disassembled and the cathode materials for thermal investigations were removed from the aluminum foil current-collector. The materials stored in a bottle were not dried, and used directly as such for carrying out TGA and DSC experiments.

DSC-Q1000 and TGA-Q600 from TA Instrument USA which use data processing program universal analysis 2000 were used for carrying out the DSC and TGA analysis of the samples. The sample holders are made up of alumina and aluminum for DGA and DSC, respectively. Electrode material weighing ~8 to 10 mg was kept in open alumina holder and ~7–9 mg was crimp sealed in aluminum holder; both experiments were carried out at a scan rate of 5°C min^{-1} in a nitrogen atmosphere. The cell opening and extraction of the cathode material for these experiments were carried out in a dry-room maintained at $\sim 21^\circ\text{C}$ with dew point temperature $\sim -65^\circ\text{C}$. A portion of the electrode cut in size $20\text{ mm} \times 10\text{ mm}$ 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). IC was also carried out for a solution prepared by adding 1 ml of the battery electrolyte (1.12 M LiPF_6 in VC/EC/EMC) in 9 ml of water giving a rest time of 30 min in order to find out the presence of other ions present in the electrolyte.

3. Results and discussion

3.1. Thermogravimetric analysis

The thermal decomposition of Li_xCoO_2 in the region above 125°C may be presented by the equation:



In the overcharged cathodes, Li_xCoO_2 exists in high de-lithiated state. As $x \rightarrow 0$ the cathode becomes more unstable, the decomposition of which at high temperature leads to the formation of LiCoO_2 , Co_3O_4 and O_2 . The decomposition follows exponential relationship with temperature [10] and the cathodes of the cell charged to above 4.2 V will be highly unstable [3]. The TGA curves obtained for electrodes charged to different temperature are presented as Fig. 1. The figure shows the weight loss occurs in three different regions. In the region around 100°C where the weight loss may either be due to evaporation of the electrolyte solvent or combination of evaporation of the solvent and weight loss due to oxidation reaction. If there is exothermic energy release in any region that will be understood from the DSC data. In the region between 200 and 400°C , the weight loss is attributed to decomposition of Li_xCoO_2 into LiCoO_2 , Co_3O_4 and oxygen. The reduction of Co_3O_4 into lower cobalt oxide or to cobalt depends on the extent of electrolyte solvent present in the sample. The liberated oxygen oxidizes the carbonaceous materials releasing carbon dioxide and energy. MacNeil and Dahn [8] analyzed the XRD pattern of $\text{Li}_{0.5}\text{CoO}_2$ sample heated with and without organic solvent using ARC and demonstrated that the former one even at lower temperature (275°C), not only produces LiCoO_2 and Co_3O_4 but also shows the presence of $\text{Li}_x\text{Co}_{(1-x)}\text{O}$. Since the amount of lithium (Li) is very small, the authors refer $\text{Li}_x\text{Co}_{(1-x)}\text{O}$ as CoO. TGA in Fig. 1 shows that the highly charged electrode materials of 4.20 and 4.35 V cells to undergo pronounced weight loss compared

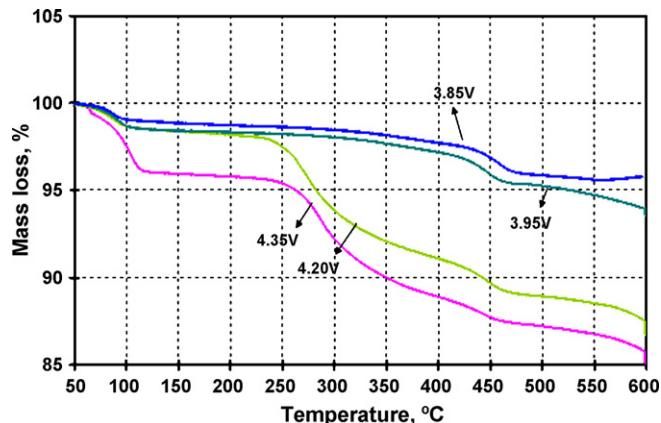


Fig. 1. TGA curves for the different cathode materials.

to electrode materials of cells charged to lower voltage cells (3.85 and 3.95 V). The highly charged material with low value of lithium could behave well like an oxidizing agent towards the electrolyte which may lead to the formation of less quantity of LiCoO_2 and Co_3O_4 , but with larger proportion of CoO.

3.2. Differential scanning calorimetry

The DSC spectrums representing the heat flow with temperature for the charged cathode are presented as Fig. 2. The figure shows that the cathodes of cells charged to 3.85 and 3.95 V have no thermal peaks in the low temperature region whereas the cells charged to 4.20 and 4.35 V have well defined exothermic peaks of the order of 4.9 and 7.0 J g^{-1} , respectively, below 100°C . Even though the intensity of these peaks is low, they arouse more curiosity as no such peaks in this temperature region have so far been reported. MacNeil and Dahn made in-depth thermal study of the cathode materials with calculated quantity of organic solvents. In this present study the cathode material containing electrolyte as removed from the cell was explored for obtaining thermal data. The thermal exothermic energy released is assumed to be due to the reaction between the oxide cathode material and the organic electrolyte present in it. The heat energy calculated from the DSC spectrum for the cathode materials are 83 and 80 J g^{-1} between 125 and 250°C and above 250°C the values are 81 and 17 J g^{-1} for the respective cathode materials of 4.20 and 4.35 V cells. The lower exothermic energy release of cathode material of 4.35 V cells at higher temperature region may be associated with early history of the sample such as decomposition of the cathode material/electrolyte during over-

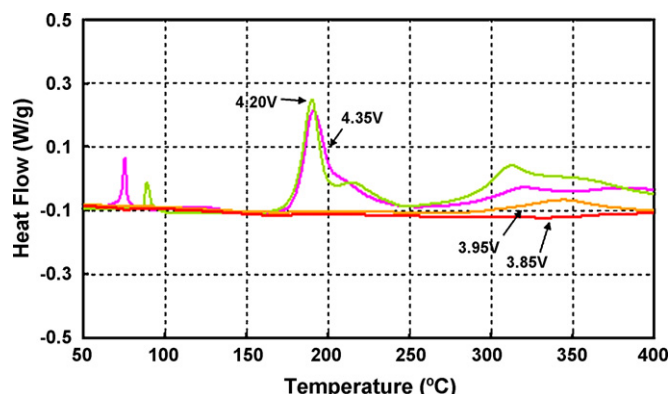


Fig. 2. DSC scans for the cathodes of 3.85, 3.95, 4.20, and 4.35 V cells.

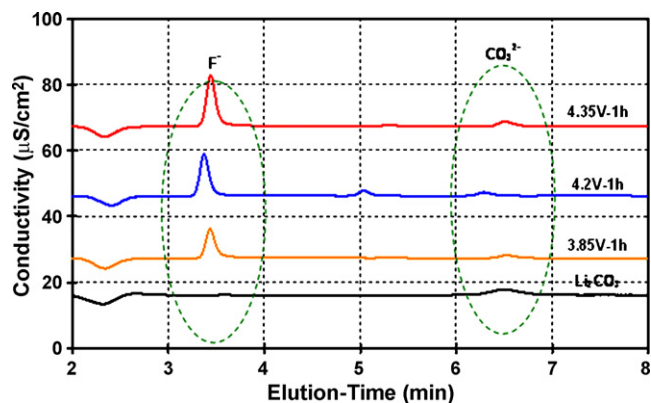


Fig. 3. Ion chromatography of the solution: the electrodes dipped in distilled water; Li_2CO_3 dissolved in distilled water.

charging and decomposition at low temperature region in DSC itself.

3.3. Ion chromatography

Dedryvère et al. identified, using XPS spectra of the positive electrode of LiCoO_2/C cell charged to different cell voltages, a passivation film of LiF on the surface of positive electrode material which increased progressively from $\sim 10\%$ at 3 V up to 18% at 4.2 V [6]. Presence of ionic carbonate in the electrodes was identified by immersing the electrode in distilled water for 1 h using IC technique and presented as Fig. 3. 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. Again in order to clarify the origin of the peak at 5 min elution time for the 4.2 V 1 h, 1 ml of fresh battery electrolyte (1.12 M LiPF_6 in VC/EC/EMC) added to 9 ml of distilled water with a 30 min rest time was analyzed and presented in Fig. 4. The figure shows the probable ionic species which may get incorporated in the electrode materials. Comparison of Figs. 3 and 4 shows the peak at 5 min elution time in the IC of 4.2 V 1 h sample is due to the presence of chloride impurities present in the electrolyte. Hence it may be concluded that the possible materials present over the surface of the electrode material are LiF , Li_2CO_3 and trace quantity of LiCl . Even though LiCl could have same role as LiF , only LiF is considered for discussion as the contribution of LiF will be greater compared to LiCl .

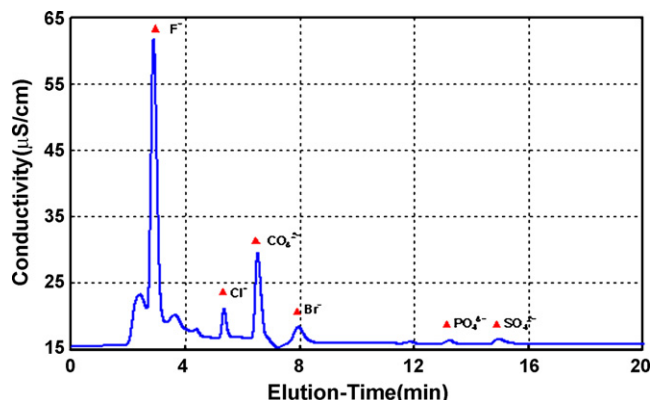
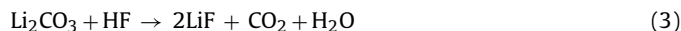


Fig. 4. Ion chromatography of the electrolyte added to distilled water.

3.4. Mechanism of SEI film break down

The following two reactions may be visualized to take place consecutively around 100°C . At first proton is released [7] from the organic solvent due to the weak interaction between the positive electrode materials and organic solvent which then reacts with LiF leading to the formation of HF . 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 which could allow easy diffusion of the available organic 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 [11,12]. Such unstable positive electrode [3,13] could be expected to react with the organic solvent releasing proton. Following this, the HF formation and its reaction with carbonates in the SEI layer could be conceived as to cause a surge of organic solvent toward highly reactive oxide cathode releasing an exothermic heat flow of low magnitude even at low temperature region near 100°C . This explanation may be compared with the experimental findings reported in the earlier that only highly charged batteries are prone to explosion during battery abuses [3].

4. 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 in DSC experiments. The cause for the appearance of the exothermic peak is visualized as due to disruption of the SEI film, thermally induced by acidic environment shifting solid SEI phase into liquid leading to easy access of the organic solvent of the electrolyte to the surface of the cathode. The formation of HF and the high oxidation state of the cathode may be considered responsible for the appearance exothermic peak around 100°C . The extent of this initial energy release may be assumed to play a role in triggering chain of other processes leading to battery explosion during battery abuse conditions.

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