Short communication

Thermal and electrochemical behaviour of C/Li$_x$CoO$_2$ cell during safety test

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Abstract

Thermal and electrochemical processes in a 1000 mAh lithium-ion pouch cell with a graphite anode and a Li$_x$CoO$_2$ cathode during a safety test are examined. In overcharge tests, the forced current shifts the cell voltage to above 4.2 V. This causes a cell charged at the 1 C rate to lose cycleability and a cell charged at the 3 C rate to undergo explosion. In nail penetration and impact tests, a high discharge current passing through the cells gives rise to thermal runaway. These overcharge and high discharge currents promote joule heat within the cells and leads to decomposition and release of oxygen from the de-lithiated Li$_x$CoO$_2$ and combustion of carbonaceous materials. X-ray diffraction analysis reveals the presence of Co$_3$O$_4$ in the cathode material of a 4.5 V cell heated to 400 °C. The major cathode product formed after the combustion process cells abused by forced current is Co$_3$O$_4$ and by discharge current the products are LiCoO$_2$ and Co$_3$O$_4$. The formation of a trace quantity of CoO through the reduction of Co$_3$O$_4$ by virtue of the reducing power of the organic solvent is also discussed.
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1. Introduction

Lithium-ion battery technology with graphite and Li$_x$CO$_2$ electrode materials has been widely used as a power source for portable electronics [1]. In the recent past, however, a widespread recall of batteries affected nearly 10 million products when it was found that some batteries were causing notebook computers to overheat and, in some cases, gave rise to a fire [2]. Followed by this, safety became the password of the lithium-ion battery and it became mandatory for any particular company to evaluate and assure the quality of their product. In order to evaluate and improve the safety standards of lithium-ion batteries, abuse tests procedures have been formulated by the Underwriters Laboratories (UL-1642), the United States Advanced Battery Consortium (USABC), the Electrochemical Storage System Abuse Test Procedure Manual, and the Japan Storage Battery Association (JBA) [3,4]. Subsequently, there have been many safety-related studies, suggestions on protection mechanism, and attempts to develop new coatings over cathode materials to provide more thermal stability and safety [5–16].

During abuse tests of a prismatic cell (600 mAh), Toshiba and yamaki [4] found that overcharging at the 2 C rated to a fire, whereas thermal investigations showed that most of the uncycled cells produced smoke and became thermally unstable above 150 °C [4]. It was proposed that this behaviour was due to exothermic reactions such as the chemical reduction of the electrolyte by the anode, oxidation of the electrolyte by the cathode, and thermal decomposition of the anode, electrolyte and cathode. Through spot-weld tests for a cell with a Li$_x$CoO$_2$ cathode and a dimethoxymethane (DME) based electrolyte, Wainwright [6] observed a violent venting when $x = 0.4$ but could not vent

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for $x = 0.5$, even when the spot heating was sufficient to melt and breach the container. Through simulation studies, it was concluded that thermal runaway of a single cell could induce thermal runaway of a computer pack containing eight cells when the cells were closely packed [16].

In this study, we discuss the processes that occur in 1000 mAh lithium-ion pouch cells during abuse tests such as overcharge, nail penetration and impact tests. A thorough discussion of the polarization and combustion process during such treatment is made by considering the previous literature together with XRD analysis of a heat-treated cathode of the 4.5 V type to explain the possible course of reaction.

2. Experimental

2.1. Pouch cell construction

The safety tests were performed on a commercial, rectangular, pouch cell (1000 mAh) of dimensions 60 mm × 33 mm × 4 mm received from a manufacturing company. 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 aluminium current-collector in the weight ratio of 94, 3, and 3%, respectively. The particle size of Li_xCoO_2 is 20 μm. The anode material constituents were coated over a copper current-collector and comprised a blend made up of mesocarbon microbeads and PVDF in a weight ratio of 92 and 8%. The electrolyte was 1.12 M $LiPF_6$ dissolved in a mixture of solvents, namely, ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). The cells required for the tests were charged/overcharged by means of a Digatron (Germany) charger. Details such as the origin of the separator and the exact ratio of organic solvents were not provided in the cell manufactuer's data sheet.

2.2. Instrumental procedures

The pouch cells were overcharged/charged to a set voltage value either for heat-treatment experiments or for abuse tests. During the latter tests, the temperature variation with time was recorded by means of an electronic digital recorder with a thermocouple probe fixed tightly over the surface of the test cells. Designed and locally fabricated equipment was employed for carrying out the nail penetration and the impact tests. The nail penetration test was performed using a nail (50 mm long, 5 mm diameter) at a penetration rate of 5 mm s^{-1} at the centre of the cell which was placed on an iron plate in a closed chamber. The impact test was carried out by placing a rod (15.8 mm diameter and 50 mm length) on the cell which was kept on a flat iron plate and over that an iron cylinder ($\sim$15 cm × 10 cm) weighing 9.1 kg was allowed to fall from a height of $\sim$610 mm onto the cell. The overcharge test and nail penetration test chambers were each provided with a glass door to view the experiments. In order to have an insight into the materials formed during abuse tests, a pouch cell was charged up to a cut-off voltage of 4.5 V. The cell was dissembled and the active material coated over the

aluminium foil was excised and collected. The material was then heated under an argon atmosphere at a rate of 5 °C min^{-1} so as to reach a temperature of 400 °C. The heating was then switched off to cool the cell down spontaneously to room temperature. A heating temperature of 400 °C was chosen as this is close to the temperature range of the pouch cell during explosion or near explosion. Also, the observation [17] that the internal cell temperature of abused cells is always higher by 80 °C over that of the surface of the cell has also been taken into consideration. A Philips 1830 X-ray diffractometer with nickel-filtered Cu Kα radiation at a scan rate of 0.04° s^{-1}. over a 2θ range of 10–80° was used to analyze the cathode material heated to 400 °C.

3. Results and discussion

3.1. Thermal analysis

The thermal decomposition of Li_xCoO_2 may be represented by the equation:

$$Li_xCoO_2 \rightarrow xLiCoO_2 + \left(\frac{1-x}{3}\right) Co_3O_4 + \left(\frac{1-x}{3}\right) O_2 \tag{1}$$
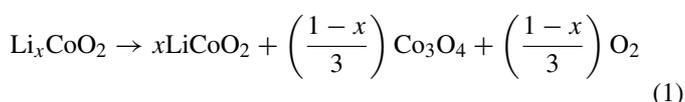
This shows that highly de-lithiated Li_xCoO_2, as in the case of overcharged cathodes where $x \rightarrow 0$, can decompose into Co_3O_4 and O_2 gas. In a partially delithiated cathode, as in the case of $Li_{0.5}CoO_2$ (4.2 V cells), the possible products are $LiCoO_2$, Co_3O_4 and O_2 gas. The XRD patterns of unheated (4.5 V cell), heated (4.5 V cell) and $LiCoO_2$ (3 V cell for comparison) cathodes are presented in Fig. 1. The Bragg peaks appearing for the unheated cathode of 4.5 V cell show a change in the crystal parameters for $LiCoO_2$, which can possibly be attributed to a de-lithiated state. After heat treatment, the XRD pattern shows the disappearance of many peaks corresponding to the parent sample. The resultant material after heat treatment has lost its crystallinity, as evident from the XRD pattern. The Bragg peaks of Co_3O_4 and $LiCoO_2$ overlap in many areas, except in the region of the Co_3O_4 (2 2 0) peak near 31.3°. The appearance of this peak in the heat-treated sample confirms the formation Co_3O_4 upon decomposition of Li_xCoO_2 [18]. The effective conversion of Co_3O_4 into CoO by the reductive action of organic solvent becomes unlikely due
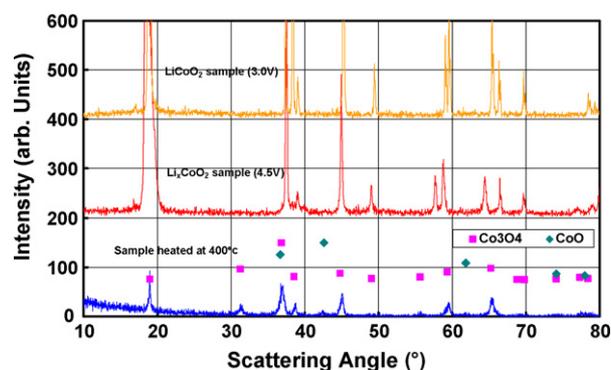

Fig. 1. XRD patterns of cathodes $LiCoO_2$ (3 V cell), Li_xCoO_2 (4.5 V cell) and heat-treated cathode (4.5 V cell) at 400 °C.

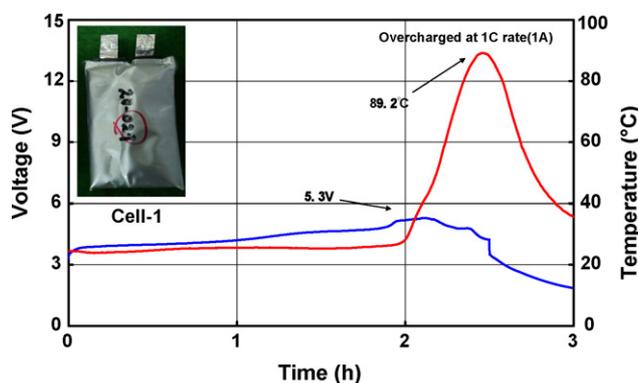Fig. 2. Voltage and thermal behaviour of Cell-1 on overcharge at 1 C rate.

Fig. 3. Voltage and thermal behaviour of Cell-2 on overcharge at 3 C rate.

to the evaporation of organic solvent. On the other hand, the probability of the formation of a trace quantity of CoO from the reduction of Co_3O_4 by the carbonaceous residues present in the cathode material may be attributed to the weak peak appearing in the XRD pattern. The formation of $LiCoO_2$, Co_3O_4 and CoO has been reported [18,19] from a thermal study carried out for $Li_{0.5}CoO_2$ with electrolyte. Since all the abuse-tested cells contain electrolyte, it is expected that the formation of a small quantity of CoO occurs from the reduction of Co_3O_4 by virtue of the reducing power of the solvent [19]. Dahn et al. [20] investigated the thermal behaviour of Li_xCoO_2, Li_xNiO_2, and $Li_xMn_2O_4$ materials and found that the amount of oxygen released into the electrolyte increases with decrease in the x value. Hence a highly oxidized cathode could explode violently as the amount of oxygen released from the combustion reaction is enormous.

3.2. Overcharge at 1 C rate

The overcharge behaviour of a pouch cell designated as Cell-1 at the 1 C rate for 2.5 h is presented in Fig. 2 along with photograph of the abused cell. During the first hour, the cell voltage shifts from 4.2 to 4.5 V. This will cause the electrode to polarize and give rise to the following process. As the potential of the Li_xCoO_2 electrode shifts to a more positive value and de-intercalation of lithium ions proceeds along with the oxidation of Co^{3+} into unstable Co^{4+}, which dissolves in the electrolyte. The dissolution of Co^{4+} accelerates with time as the potential shifts to more positive values and results in damage to the Li_xCoO_2 crystal, a process which is related to fading of cell capacity [21]. The polarization process is followed by a thermal process. As the x value in Li_xCoO_2 shifts from 0.45 to 0.3, a large anisotropic volume change of 3% occurs due to the phase transition between hexagonal and monoclinic H1-3 phases [22,23]. Such a crystal-phase change is also presumed to induce thermal instability of the positive electrode [24]. As the cathode is completely de-lithiated, the cell voltages moves above 4.5 V, the ionic conduction completely ceases, and the passage of current through the cell becomes purely ohmic resulting in heat generation due to I^2R loss. The poor heat dissipation of the cell components causes an exponential increase in cell temperature
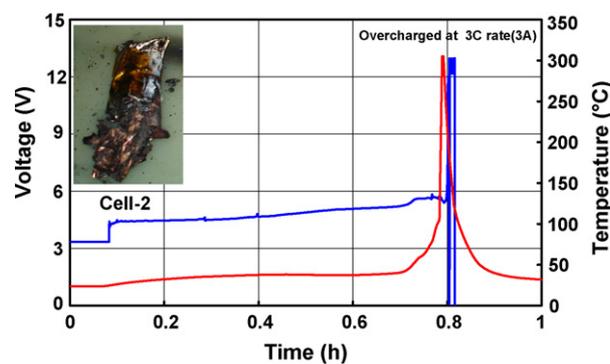
[24], which induces decomposition of Li_xCoO_2 according to Eq. (1). As discussed in Section 3.1, for the overcharged cathode Li_xCoO_2 where $x \rightarrow 0$ the decomposition will lead to the formation of Co_3O_4 and oxygen [20]. At higher temperatures, the liberated oxygen and the Co_3O_4 promotes combustion of carbonaceous materials. Since the cell contains electrolyte, Co_3O_4 will be reduced to CoO [18]. The extent of conversion depends on the probability of contact between Co_3O_4 and the reductive organic species available during the combustion process. Fig. 2 also shows an abrupt triggering of heat after 2 h of charging, which is possibly due to meltdown of the separator ($\sim$125 °C for polyethylene and $\sim$155 °C for polypropylene) [4] leading to a cell short-circuit. As the passage of overcharge current ends at 2.5 h, the joule heating also ceases. Finally, both cell voltage and temperature start decline from the peak values of 5.3 V and 89 °C, respectively. As reported [17], the inner cell temperature will be 169 °C. The disconnected battery from the abuse tests was subjected to charge but it was found that the cell could not be recharged and has undergone thermal runaway.

3.3. Overcharge at 3 C rate

The overcharge behaviour of the pouch cell designated as Cell-2 recorded at 3 C rate (current-3 A) and a photograph of cell used for the tests are presented in Fig. 3. After 0.7 h, there appears to be a change in both the voltage and the temperature behaviour of the cell. At the $\sim$0.8 h, the cell temperature and voltage move above 300 °C and 12 V, respectively. The sudden drop of cell voltage after reaching 12 V implies perfect shorting of the electrodes, possibly due to meltdown of the separator. The temperature and the cell voltage are so high to cause the process (described for the Cell-1) for the cell destruction. Meltdown of the separator and combustion of the organic electrolyte with the release of oxygen would have been instantaneous to cause volume expansion and violent explosion. The maximum dc power attained is $\sim$39 W and the cell surface temperature reaches 300 °C.

3.4. Nail penetration test

A cell designated as Cell-3 was subjected to nail penetration and a photograph of the cell taken after the test is presented in
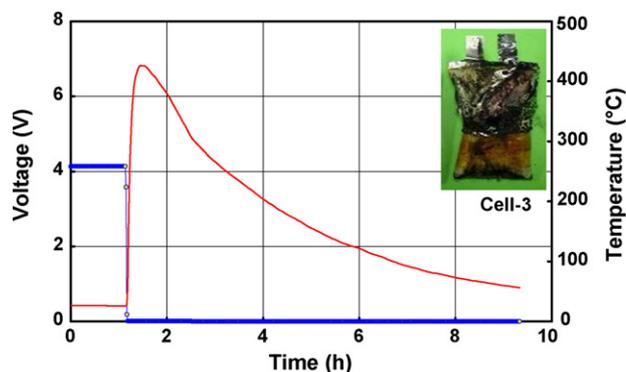
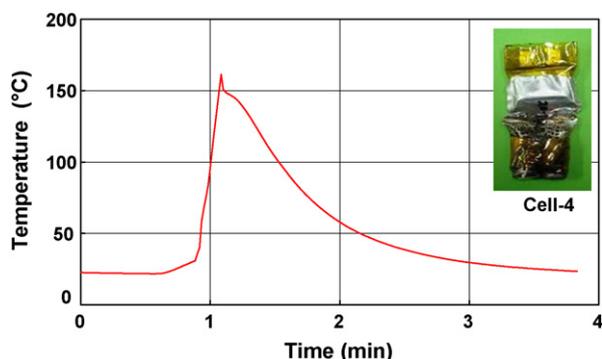Fig. 4. Voltage and thermal behaviour of Cell-3 on nail penetration test.

Fig. 5. Thermal behaviour of Cell-4 on impact test.

Fig. 4. The figure also shows a constant voltage and temperature before the tests are conducted. At the instant the experiment started, however, the voltage falls to zero and the surface temperature of the cell shoots up to $420\,°C$, which could only be attributed to a high surge of discharge current resulting in a high joule heat followed by separator meltdown and contact of the anode and the cathode. In the case of overcharge tests, the electrodes are charged at a known external current, whereas, in nail penetration tests the quantity of the discharge current flowing through the nail is not known. The temperature of the cell reaching $420\,°C$ shows that the intensity of the discharge current in the nail penetration test could have been much higher than that in overcharge test. The current flowing through the nail can be compared with well-known dendrite shorting. The usual discharge product $LiCoO_2$, along with Co_3O_4 and O_2 gas from the decomposition of de-lithiated cathode Li_xCoO_2, could be expected, after combustion process. In addition, a trace quantity of CoO could also be expected, as explained in Section 3.1. The cell does not explode violently as the nail has made a partial way for the release of gaseous materials and the cell appears to have expanded as evident from the figure (Fig. 4).

3.5. Impact tests

The thermal behaviour along with a photograph of the impact tested cell designated as Cell-4 is presented in Fig. 5. In nail penetration tests, the nail makes a direct contact between the anode

and cathode. But in the impact tests, the cylindrical rod is kept horizontally over the cell which crushes the cell at the centre. Such action is expected to expand and tear the separator that makes contact between the positive and negative electrodes. A high discharge current will flow between the anode and cathode of the cell. The highest surface temperature noted is $161\,°C$ (the internal temperature will be around $241\,°C$). As the internal portion of the cell is opened the gaseous products formed will be easily released from the cell and these will be less severe effect on the environment.

4. Conclusions

In overcharged cells, the forced current causes polarization of the electrodes and induces release of Li^+, Co^{4+} and oxygen from the positive electrode. As $x \to 0$ in Li_xCO_2 when the cell shifts above $4.5\,V$, ionic current tends to cease and the current flow passing through the cell becomes purely ohmic and causes heat generation due to I^2R loss. This heat decomposes the charged cathode particles into Co_3O_4 and oxygen. In nail penetration and impact tests the high discharge current produces $LiCoO_2$ and the joule heat developed during discharge process disintegrates de-lithiated $LiCoO_2$ into Co_3O_4 and oxygen. The oxygen gas thus formed gives rise to a combustion reaction with the carbonaceous material and there by results in thermal runaway in some cells and violent explosion in others. Also, there may be formation of CoO from the reduction of Co_3O_4 by the organic solvent by virtue of its reducing power in all the abused cells.

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