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Short communication

Dependence of AlPO$_4$ coating thickness on overcharge behaviour of LiCoO$_2$ cathode material at 1 and 2 C rates

Jaephil Cho[*]

Department of Applied Chemistry, Kumoh National Institute of Technology, Gumi 730701, South Korea

Abstract

The overcharge behaviour of AlPO$_4$-coated LiCoO$_2$ cathodes as a function of coating thickness is investigated in Li-ion cells at 1 and 2 C overcharging rates. The AlPO$_4$ coating thickness is controlled by the concentration of the coating solution. During 1 C-overcharging to l2 V, the 5 V plateau region, which is indicative of both electrolyte oxidation and an exothermic reaction between the electrolyte and the cathode, decreases with increasing AlPO$_4$ coating thickness (AlPO$_4$ concentration). Therefore, a Li-ion cell containing a P100-coated LiCoO$_2$ cathode (AlPO$_4$ coating thickness estimated as 1000 Å) does not show the 5 V plateau, and displays the lowest cell external temperature of 60 °C, even at 12 V. This suggests that the reaction at the 5 V plateau strongly influences the final external temperature of the cell. When a higher current is applied (2 C), cells with bare or P10-coated LiCoO$_2$ cathodes either burst or explode, and reach external temperatures of over 275 °C. By contrast, cells with P30 and P100-coated cathodes show only a swollen external appearance with temperature profiles similar to those at the 1 C-overcharging rate.
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1. Introduction

Safety is considered to be one of the most important features of Li-ion cells, and a cell that does not meet safety guidelines cannot be used in mobile applications [1,2]. To date, the capacity of cells of the same size has increased by 7% per each year. Protective devices are required to secure cell safety. In this respect, all producers of Li-ion cells have installed protecting devices in the battery pack itself or have produced batteries that block over-temperature, over-current, overcharging, and a safety pressure-release rupture or vent. Nevertheless, many safety accidents involving smoke, fire or explosions due to defects or malfunction of the devices have been reported [3,4]. Among the safety tests for Li-ion cells, an overcharge test to 12 V is the most critical according to the guidelines [1,2]. In this test, a cell is forced to charge to the limit of the power supply, 12 V. Under such conditions, a cell using LiCoO$_2$ and without any additives that retard the flammable nature of the electrolyte experienced an incendiary explosion [5]. Among the cell components, violent exothermic reactivity of the delithiated cathode with

flammable electrolytes leads to substantial heat generation, which is reported to be a trigger point for thermal runaway [6–10]. This is accompanied either by pressure build-up, which leads to bursting of the cell, or by fire due to an internal short-circuit. Therefore, the guidelines recommend that a cell that emits smoke, catches fire or explodes during the abuse tests are unacceptable for potential applications.

Several authors have reported that additives in the electrolytes can prevent thermal runaway [10–14]. It has been found that additives such as phosphorus compounds or aromatic compounds with two methyl groups can reduce the flammable nature of the electrolytes. Unfortunately, however, the electrochemical properties of the cathode and anode materials were damaged by these additives. Recently, Cho et al. [5] showed that a AlPO$_4$ nanoparticle coating on the LiCoO$_2$ cathode remarkably improves thermal stability, even at 12 V. For example, Li-ion cells with a 1600 mAh capacity did not exhibit thermal runaway during 1 C overcharging despite being short-circuited at 12 V [5]. In addition, the thermal stability of the cells was superior to that of cells with a Al$_2$O$_3$ and ZrO$_2$ coating of the cathode derived from a sol–gel method [15–17].

In this communication, the dependence of the overcharge behaviour of LiCoO$_2$ cathode material on AlPO$_4$ coating thickness is investigated for overcharge at the 1 and 2 C

* Tel.: +82-54-467-4462; fax: +82-54-467-4477.
E-mail address: jpcho@kumoh.ac.kr (J. Cho).

rates. The temperature of the cell surface is monitored using a type K thermocouple attached to the centre of the largest face of the prismatic cell.

2. Experimental

A coating solution of dispersed AlPO$_4$ nanoparticles was prepared by dissolving Al(NO$_3$)$_3$·9H$_2$O and (NH$_4$)$_2$HPO$_4$ in distilled water [18]. LiCoO$_2$ powders with an average particle size of 10 μm (BET surface area of 0.2 m^2 g^{-1}) were then added slowly to the coating solution. After mixing the slurry thoroughly, it was dried in an oven at l20 °C for 10 h, and fired at 700 °C for 5 h in a furnace. The AlPO$_4$ coating thickness was controlled by varying the concentration of the coating solution. The AlPO$_4$ coating thickness prepared from 1 g of Al(NO$_3$)$_3$·9H$_2$O and 0.38 g of (NH$_4$)$_2$HPO$_4$ was observed by auger electron spectroscopy (AES) to be 50 Å. Henceforth, this is referred to as a P10-coated LiCoO$_2$ cathode. In order to prepare P30 and P100-coated cathodes, the weight of each of the starting chemicals was multiplied by 3 and 10 from that used in the P10 coating solution. The AlPO$_4$ coating thickness of P30 and P100-coated cathodes were observed to be approximately 200 and 1000 Å, respectively, as confirmed by TEM [5] and AES. The standard capacity of the Li-ion cell was set to 900 mAh (cell size: 3.5 mm × 65 mm × 50 mm (thickness × length × width)). Either the AlPO$_4$ nanoparticle-coated LiCoO$_2$ or bare LiCoO$_2$ was used as the cathode, and the anode material was synthetic graphite. The dimensional ratio of the anode to cathode was set at 1.2. The electrolyte used was 1.03 M LIPF$_6$ with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (3/3/4 vol.%). For the 1 and 2 C overcharge experiments to 12 V, fresh cells were initially cycled at a 0.2 C rate for 1 cycle, and charged to 4.2 V with a constant current corresponding to 1 C (900 mA). This was followed by holding the cell at 4.2 V until the current decreased to 30 mA. Subsequently, the cells were charged to 12 V at a rate of 1 C (equivalent to 140 mA/g = 0.9 Å) using an identical charging method to 4.2 V. In order to evaluate the thermal stability of the delithiated Li$_x$CoO$_2$ at 4.3 V (corresponding to 4.45 V versus Li metal), the fresh cells were cycled initially at a 0.2 C rate and charged to 4.3 V. Finally, the charged cells were kept in a hot oven at 150 °C for 75 min.

3. Results and discussion

The voltage and temperature profiles of cells with bare and P10, 30, 100-coated LiCoO$_2$ cathodes as a function of time at the 1 overcharging rate to 12 V are shown in Fig. 1. During 1 C overcharging, a plateau at 5 V in the cell which contained the bare cathode is observed. This is related to electrolyte oxidation and a reaction between the electrolyte and the cathode. The plateau region decreases with increase in the thickness of the AlPO$_4$ coating. Since the chemical
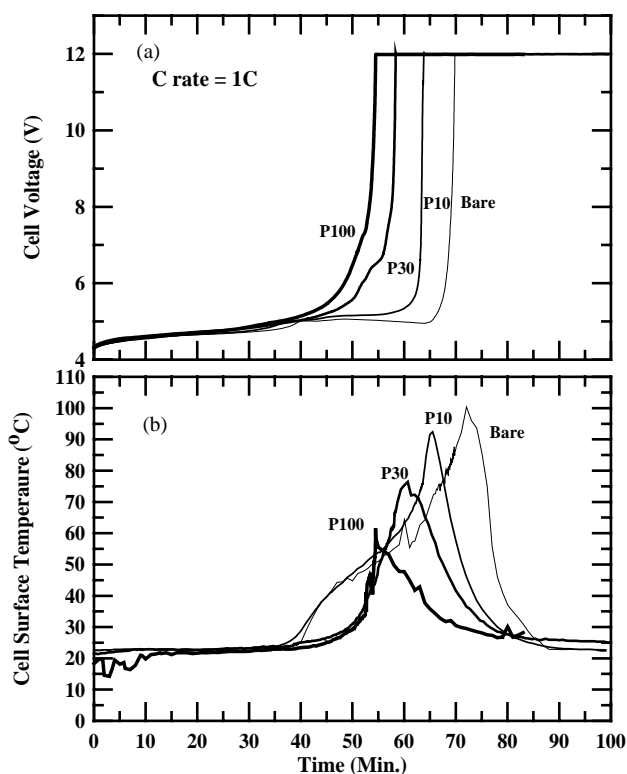

Fig. 1. Plots of (a) cell voltage curves of Li-ion cells with bare and AlPO$_4$-coated LiCoO$_2$ cathodes with different AlPO$_4$ coating thickness as function of time at 1 C rate (0.9 A) and (b) cell se temperature vs. time of cells shown in (a). Cells charged to 12 V at 1 C rate, and held at this voltage until applied current decreases to 30 mA.

reaction at 5 V is always accompanied by substantial heat generation; the degree of heat generation can be estimated by plotting the change in the cell surface temperature. The surface temperature of the cell at the 5 V plateau in the Li-ion cell which contained the bare cathode is 100 °C.

The highest temperature of the P10-coated LiCoO$_2$ is similar to that of the bare sample, but the temperatures of the P30 and P100-coated cathodes are lower, namely, 75 and 60 °C, respectively. These results indicate that a protective AlPO$_4$ coating layer is quite effective in poisoning the chemical reactions between the electrolyte and the cathode.

At the end of the 5 V plateau, there is a steep voltage increase to 12 V at which separator shut-down occurred when the internal cell temperature was >140 °C (note, a temperature difference of over 80 °C between the internal and external cell has been reported [6]). At 12 V, the surface cell temperature is strongly dependent on the AlPO$_4$ coating thickness, and the cell with the P100-coated cathode shows the lowest temperature while that with a bare sample recorded the highest surface temperature. A comparison of the maximum surface temperatures of cells with bare and AlPO$_4$-coated cathodes at 5 and 12 V is given in Fig. 2. On increasing the cell voltage from 5 to 12 V, there is an increase in temperature due to heat generation that results from the decomposition of the anode, binder and
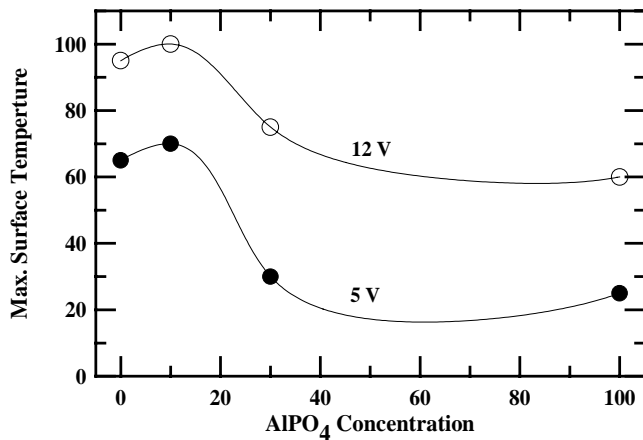
Fig. 2. Plot of the maximum cell surface temperatures at 5 and 12 V as function of AlPO$_4$ coating thickness (concentration).

lithium metal deposited on the anode, as well as an increase in internal resistance [6–8]. Nevertheless, the contribution from these is approximately 30–35 °C less than that from the reactions at 5 V, which suggests that most of the heat generation in the cell originates from decomposition of the electrolyte and the cathode.

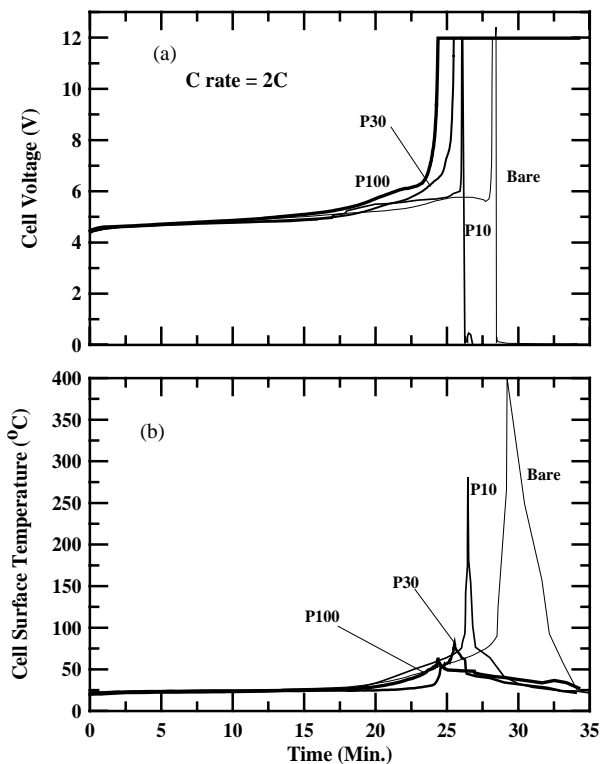At 2 C overcharging, the amount of heat generation increases proportionally with the internal resistance, i.e. with i^2R. Therefore, the rise in cell surface temperature is faster at 2 C than at 1 C, as shown in Fig. 3. At 12 V, the Li-ion cell with the bare electrode became short-circuited (voltage suddenly dropped to 0 V), and the temperature spiked to 400 °C. The anode cap housing of the cell was lost and totally burnt-out, as shown in Fig. 4a. Even though this was much less in the cell with the P10-coated cathode, the external temperature of the cell was 275 °C after being short-circuited. The safety rupture unit at the bottom of the cell was opened and soot-covered (Fig. 4b). It should be noted, however, that the cell surface temperatures of the bare and P10-coated LiCoO$_2$ cells were approximately 175 and 225 °C, respectively, before an internal-short occurred. Therefore, an internal-short resulted in a catastrophic failure of the cell.

Fig. 3. Plots of (a) cell voltage curves of Li-ion cells with bare and AlPO$_4$-coated LiCoO$_2$ cathode with different AlPO$_4$ coating thickness as a function of time at 2 C rate (1.8 A) and (b) cell surface temperature vs. time of cells in (a). Cells charged 12 V at a 2 C rate, and held at this voltage until applied current decreases to 30 mA.

Fig. 4. Pictures of cell external appearance after 2 C overcharging experiments.
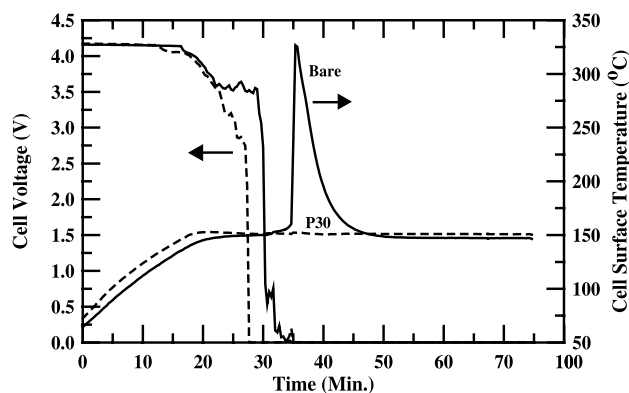
Fig. 5. Plot of change in cell surface temperature in Li-ion cells with bare and P30-coated LiCoO$_2$ cathode when exposed to 150 °C in a hot oven for 75 min.

Even though the 5 V plateau region during 2 C-overcharging was smaller than that during 1 C-overcharging in all the cells, the cell temperature rapidly increased when the cell voltage spiked at 12 V. This indicates that the reaction rate of the cathode and the electrolyte decomposition rate both increase. Despite this, the cell temperatures increase much slower in the cells with the P30 and P100-coated cathodes than that of both the bare and P10-coated cathodes without showing any short-circuit. The former only exhibit a swollen shape, as shown Fig. 4c. Accordingly, the AlPO$_4$ coating thickness plays a key role in controlling the reactivity of the delithiated cathode with the electrolytes, and only a coating thickness over 200 Å can block thermal runaway.

In addition, the thermal stability of Li-ion cells with bare and P30-coated LiCoO$_2$ cathodes at 4.3 V was compared in a hot oven set at 150 °C for 75 min, as shown in Fig. 5. The cell voltage decreases until the cell surface temperature becomes equilibrated with the oven temperature. This is due to separator meltdown. Even though the cell with the P30-coated cathode remains stable without exhibiting a temperature rise, the cell surface temperature of the cell with the bare electrode increases rapidly when the voltage is down to 0 V and reaches 325 °C after 35 min. In this case, the cell bottom rupture plate burst, as shown in Fig. 4b. Again, this experiment clearly demonstrates that an AlPO$_4$ coating layer stabilises the cathode material.

4. Conclusions

The thermal stability of the LiCoO$_2$ cathode strongly depends on the AlPO$_4$ coating thickness. As this thickness is increased, the cell safety improves even at a 2 C-overcharging rate and shows no thermal runaway. It is believed that will allow the development of a Li-ion cell that will not require a protection circuit mode (PCM). (Note, the PCM consists of a material with a positive temperature coefficient and protective circuits that block overcharging above 4.35 V, overdischarging below 2 V, and overcurrent above 1 C.)

References

[1] Guideline for the Safety Evaluation of Secondary Lithium Cells, Japan Battery Association, 1997.
[2] A Safety Standard for Lithium Batteries, UL1642, third ed., Underwriters Laboratories, 1995.
[3] Laptop Batteries are Linked to Fire Risk, US Consumer Product Safety Commission, New York Times, 15 March 2001, http://www.cpsc.gov/cpscpub).
[4] S.C. Levy, P. Bro, Battery Hazards and Accident Prevention, Plenum Press, New York, 1994.
[5] J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee, B. Park, Angew Chem. Int. Ed. 42 (2003) 1618.
[6] R.A. Leising, M.J. Palazzo, E.S. Takeuchi, K.J. Takeuchi, J. Electrochem. Soc. 148 (2001) A838.
[7] H. Maleki, S.A. Hallaj, J.R. Selman, R.B. Dinwiddie, H. Wang, J. Electrochem. Soc. 146 (1999) 947.
[8] A. Duaquier, F. Disma, T. Bowmer, A.S. Gozdz, G.G. Amatucci, J.-M. Tarascon, J. Electrochem. Soc. 145 (1998) 472.
[9] H. Maleki, G. Deng, A. Anani, J. Howard, J. Electrochem. Soc. 146 (1999) 3224.
[10] N. Takami, H. Inagaki, H. Ishii, R. Ueno, M. Kanda, in: Proceedings of the IMLB11-11th International Meeting on Lithium Batteries, 23–28 June 2002, Monterey, CA, USA.
[11] K. Xu, M.S. Ding, S. Zhang, J. Allen, T.R. Jow, J. Electrochem. Soc. 49 (2002) A622.
[12] S.C. Narang, S.C. Ventura, B.J. Dougherty, M. Zhao, S. Smedley, G. Koolpe, US Patent 5,830,660.
[13] M. Adachi, K. Tanaka, K. Sekai, J. Electrochem. Soc. 4 (1999) 1256.
[14] X. Wang, E. Yasukawa, S.J. Kasuya, Electrochem. Soc. l48 (2001) A1058.
[15] J. Cho, Y.J. Kim, T.-J. Kim, B. Park, Angew. Chem. Int. Ed. 40 (2001) 3367.
[16] J. Cho, Y.J. Kim, K.-T. Kim, B. Park, Chem. Mater. 13 (2001) 18.
[17] J. Cho, Y.J. Kim, K.-T. Kim, B. Park, Chem. Mater. 12 (2001) 3788.
[18] J. Cho, Electrochem. Commu. 5 (2003) 46.