ELSEVIER

3-Chloroanisole for overcharge protection of a Li-ion cell

Young-Gi Lee [a], Jaephil Cho [b],*

[a] *Ionics Devices Team, Electronics and Telecommunications Research Institute (ETRI), Daejeon 305-700, Republic of Korea*
[b] *Department of Applied Chemistry, Kumoh National Institute of Technology, Gumi 730-701, Republic of Korea*

Abstract

We observed that 3-chloroanisole (3CA), as an electrolyte additive was very effective for overcharging protection during a 12 V overcharging reaction. During overcharging, the cell voltage did not increase beyond 5.3 V, as opposed to other aromatic compounds that showed a voltage shoot-up to 12 V. This behavior was due to the 3CA decomposition and the formation of conducting polymer film within separator and at cathode/electrolyte interface, which consumes the surplus current and inhibit the voltage increase through the shunting effect. In addition, the use of 3CA did not lead to any problems with rate capability, cycle life, and long-term storage behavior at 50 and 70 °C. Furthermore, during storage at 90 °C for 4 and 24 h, electrolyte with 3CA in a Li-ion cell showed a similar increase of cell thickness as a cell without 3CA.
© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

The safety concern of Li-ion batteries is important for their commercial application [1–10]. In many abuse conditions, such as overcharge and short-circuit, the electrolytes react exothermally with electrodes, resulting in thermal runaway of the Li-ion cells. Most Li-ion batteries have adopted external safety system such as integrated circuit (IC) that interrupts surplus current, a pressure-activated aluminum burst disk and current breaker, and a positive temperature coefficient (PTC) device. However, they add a cost problem to Li-ion cells and also work to permanently inactivate and even damage the battery.

As the mobile electronics requires larger Li-ion capacity, the safety problem is the most critical issue of the present Li-ion batteries. Thus, an internal safety system that operates before the cell reaches the dangerous point without inactivating the battery is also desirable. There have been several reports on a built-in and chemical prevention of the overcharge, namely, electrolyte additives [11–27].

Among them, redox shuttle compounds such as *n*-butylferrocene [15], anisole and phenothiazine [16,17] as an additive consume extra current by repetitive redox reaction between cathode and anode. When the full charge voltage is exceeded,

the redox additive in the electrolyte is oxidized at the cathode, migrates to the anode, and is reduced reversibly to the original state. These reactions occur over and over to keep the voltage steady even when an overcharge current is supplied. However, they show some limit over huge current management, so they are still not sufficient to effectively prevent overcharge.

Other additives for overcharge protection are the aromatic compounds [19–22] such as biphenyl (BP) and cyclohexyl benzene (CHB), which polymerize electrochemically at the cathode/electrolyte interface. The formed polymer film seems to act as a passive layer increasing internal impedance and eventually shutting down LIBs though some controversy on their working mechanism.

In this study, we chose 3-chloroanisole (3CA) among others because it has redox potential above 4.4 V and could readily undergo further decomposition beyond 4.6 V due to its poor delocalization of lone-pair electrons in one methoxy oxygen [28,29]. We investigated 12 V overcharge test for Li-ion cell containing 3CA as a protecting electrolyte additive. In addition, its influences for rate capability, cycle life, and long-term stability under high-temperature storage are also investigated.

2. Experimental

Liquid electrolytes (1 M LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC)

(1/1/1, w/w)) (Cheil Ind., Korea) containing less than 20 ppm HF were used for electrochemical tests. 3-chloroanisole (98% purity, Aldrich) was further purified by vacuum distillation before use. The cathodes for the battery test cells (463448-size pouch type) were made from the $LiCoO_2$ cathode material, Super P carbon black, and polyvinylidene fluoride (PVdF) binder (Kureha Company) in a weight ratio of 96:2:2. The anodes for the battery test cells were made from the synthetic graphite powders, and polyvinylidene fluoride (PVdF) binder (Kureha Company) in a weight ratio of 94:6. The electrodes were prepared by coating a cathode-slurry onto an Al foil followed by drying at 130 °C for 20 min. The slurry was prepared by thoroughly mixing an N-methyl-2-pyrrolidone (NMP) solution of PVdF, carbon black, and the powdery cathode material. The test cells were aged at room temperature for 24 h prior to the electrochemical test. Li-ion cells with a nominal capacity of 700 mAh were used for the electrochemical tests and 12 V overcharging experiments. The dimensional ratio of anode to cathode of 1.08:1 was used for the Li-ion cells. The overcharge test was conducted with a constant current of 1 A. The cell-surface temperature was monitored using a K-type thermocouple placed on the center of the largest face in the cell can, and the thermocouple was tightly glued with insulating tape. For the rate capability and life cycle performance tests, the cells were charged with a constant current mode to 4.2 V and maintained at this voltage with a constant voltage mode (CV) for 5 h. For the storage tests, the cells were charged with CC mode to 4.2 V and maintained at this voltage with a constant voltage mode (CV) for 5 h. After fully charging to 4.2 V, the cells were kept at 4.2 V at various temperatures.

Cyclic voltammogram experiments were carried out with a Solartron 1287 potentiostat/galvanostat using a three-electrode cell. A 2 mm diameter Pt disk was used as the working electrode, a Pt plate as counter electrode, and lithium pressed on a SUS strip was used as a reference electrode. The potentials are shown in reference to the lithium versus Li/Li^+. The scan rate for linear sweep voltammetry (LSV) experiment was 2 mV/s. The ^1H NMR spectra were obtained in dimethylsulfoxide (DMSO-d_6) or chloroform-d ($CDCl_3$) solvent on a Bruker-AMX 500 NMR spectrometer with tetramethylsilane (TMS) as an internal standard.

3. Results and discussion

Fig. 1 shows profiles of cell voltage and cell surface temperature during the overcharging test using Li-ion cells containing electrolytes without 3CA and with 3 and 5 wt.% 3CA. One main feature of Fig. 1(a) during the overcharge test is the steep voltage uprise above 6 V (up to 12 V). The internal temperature can increase above the melting temperature of polymer separator ($T_m = 120–150$ °C), accompanied by a separator shutdown and a rapid increase in the cell resistance. Moreover, further increase of internal temperature even can melt down separator and the Li metal ($T_m = 180$ °C) deposited on the anode. Then, the cell leads to internal short circuit in the end as shown in Fig. 1(a). After 25 min cell voltage abruptly decreases to almost 0 V. Therefore, an internal short circuit resulted from overcharging directly leading to the thermal runaway of the Li-ion cell,
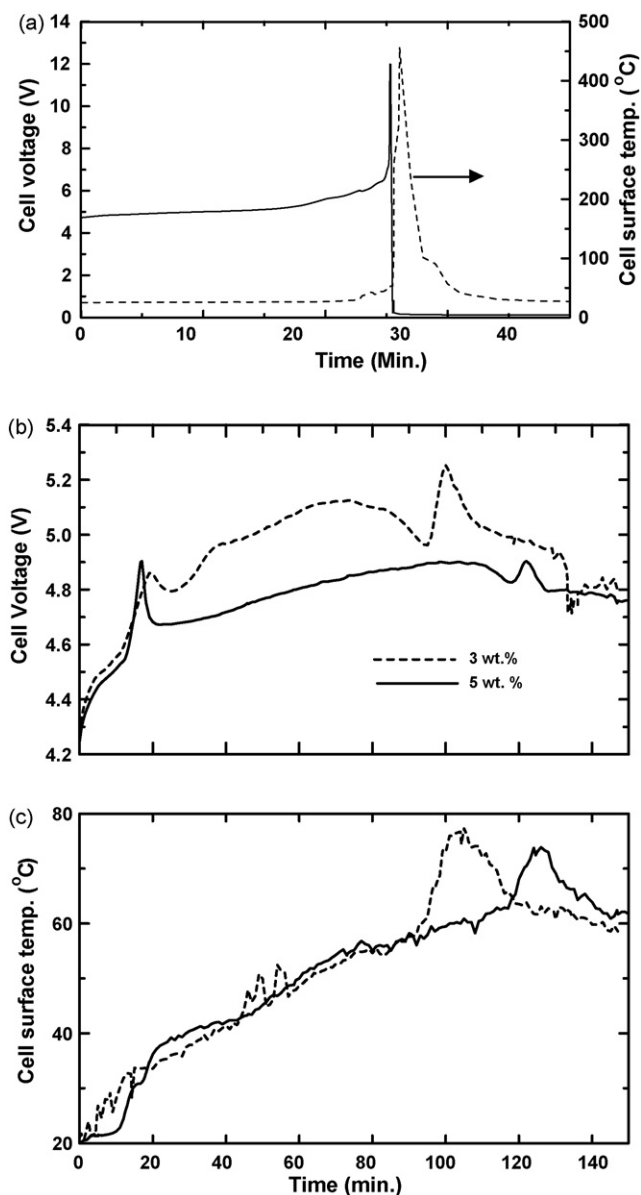

Fig. 1. Profiles of cell voltage during 12 V overcharging test for using Li-ion cells containing electrolytes: (a) without 3CA, (b) with 3 and 5 wt.% 3CA, and (c) cell-surface temperatures of (a) and (b).

accompanied with a fire and an explosion. In addition, melting of the deposited lithium metal significantly accelerated the thermal runaway of the cell. After shoot-up to 12 V, the voltage profile of the cell without 3CA shows a sharp drop to 0 V with a maximum cell-surface temperature of approximately 450 °C. This study found that the five tested cells were destroyed and covered with soot as a result of fire and explosion. This is due to an instant internal short-circuit of the cell after the 12 V maximum. On the other hand, cells containing 3 wt.% 3CA did not show an increase of cell voltage over 5.3 V and the cell surface temperatures did not increase over 80 °C. As can be seen in Fig. 1(b), after a less abrupt voltage increase up to 4.9 V compared to Fig. 1(a), the voltage was sustained below 5.3 V for the entire 150 min. Coinciding with this, the cell-surface temperature reached its maximum of 80 °C around 100 and 120 min