



Possible use of methylbenzenes as electrolyte additives for improving the overcharge tolerances of Li-ion batteries

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Abstract

Based on the voltammetric behaviour of a series of methyl-substituted benzenes in 1 M LiPF₆/EC-DMC electrolyte, xylene was selected and tested as an electrolyte additive for overcharge protection of Li-ion batteries. From the overcharge curves, CV behaviour and SEM observations of the cells in the presence of xylene, it was found that the additive can polymerize at the overcharged voltage to form a dense layer of isolating polymer film at the cathode surface, which blocks off further oxidation of the electroactive material and electrolyte and, therefore, improves the overcharge tolerance of the Li-ion battery. In addition, the xylene additive has shown only a slight influence on the cycling behaviour.

1. Introduction

Lithium ion batteries are now widely used as power sources in various portable electronic applications. These batteries are constructed with highly reactive electrodes and flammable organic electrolytes, therefore possessing potentially unsafe properties compared with aqueous batteries. Most of the hazardous behaviour for the batteries was reported to arise from thermal runaway at overcharged states, due to a number of highly exothermic reactions, such as the electrolyte oxidation [1–3] and the decomposition of the cathode material [4–6], taking place in the overcharged cathode.

To ensure battery safety, commercial lithium ion batteries are equipped with external protection devices that interrupt the charging reaction when the battery voltage, internal pressure or temperature reaches a limiting value. These devices may not be able to respond when the hazardous reactions occur suddenly.

In recent years, various self-actuating mechanisms were studied for internal overcharge protection of lithium ion batteries. Redox additives were firstly reported to operate as a redox couple shuttling between the cathode and anode to shunt charging current [7, 8]. However, the additives reported so far do not operate effectively at required charging rates because of their poor solubilities and low diffusion coefficients in the organic electrolyte. Some fire-retardants are also reported as electrolyte additives to reduce the flammability of the electrolyte, but this type of additive has negative effects on battery performance due to their reactivity with the electrode active materials [9–11]. Polymerizable

additives, which can electrochemically polymerize at an overcharged cathode, are also attractive because the polymerization reaction can effectively block off the overcharging reactions to protect the batteries from hazardous damage. Up to the present, however, only a few additives of this type have been reported along with the working mechanism and influences on the performance characteristics [12, 13].

In this work, we investigated the electrochemical polymerization behaviour of methyl-substituted benzene (MB) at overcharged LiCoO₂ cathode and described the safety behaviour of the compounds as electrolyte additives for overcharge protection and their impact on the charge–discharge performances.

2. Experimental details

The benzene and its methyl derivatives (toluene, xylene and 1,2,4-trimethylbenzene) were all of analytical grade, purchased from Shanghai Chemical Reagent Corporation, and purified by washing with sulfuric acid (analytical grade), distilled water, 5% Na₂CO₃ solution and distilled water successively, then dried with calcium chloride, and finally distilled after refluxed with sodium. The 1,2,4,5-tetramethylbenzene (Ackos Organics) was used as received without further purification. The blank electrolyte used was 1 M LiPF₆ dissolved in a 1:1 mixture (by weight) of ethylene carbonate (EC) and dimethyl carbonate (DMC) purchased from Merck.

The cyclic voltammograms (CV) of the MB monomers were examined by the Pt microdisk electrode and

the powder LiCoO_2 microelectrode. The method for microelectrode preparation has been described [14]. The microelectrode voltammetry was performed on a two-electrode cell using a larger lithium sheet as both counter electrode and reference electrode and carried out on a CHI660 electrochemical workstation (Shanghai, China).

The practical Li-ion batteries used for safety tests were prismatic graphite– LiCoO_2 batteries with a nominal capacity of 800 mA h, provided by the Fenghua Lithium Battery Corporation (Guangdong, China). The changes in the impedances of the cells during charging and overcharging were measured using an HIOKI3555 Milliohmmeter (Japan). The morphological changes at LiCoO_2 electrodes after overcharge were examined by Scanning Electron Microscopy (SEM) on an ISI-SE-40 microscope (Japan).

3. Results and discussion

3.1. Choice of polymerizable additives

For most commercial lithium ion batteries, the full charge of the cathodes (such as LiCoO_2 and LiMn_2O_4) completes at 4.3 V and the oxidative decomposition of the electrolyte appears at about 5 V. Thus, in order to avoid electrolyte decomposition and to ensure the charging completion of the cathodes, the monomer additives must be able to polymerize in the potential region just above 4.3 V and below 5.0 V. From kinetic considerations, the electrooxidative polymerization of the additives should proceed at sufficiently high rate to provide effective hindrance for the electrochemical oxidations of cathodic materials and electrolyte. On the other hand, the additives must not have significant negative influences on the normal charge–discharge performances.

Figure 1 shows the CV curves obtained from a Pt microdisc electrode in 1 M LiPF_6/EC -DMC electrolyte containing 5 wt % benzene and its derivatives, respectively. All the compounds tested show remarkable oxidation peaks in the potential region of 4.3–5.0 V in the first anodic scan and there are no corresponding reduction peaks in the reverse scan. Also, the oxidation peaks only appear in the first anodic scan and diminish or totally disappear during successive scans. Considering the feasible polymerization of benzene derivatives at positive potentials [15, 16] and the irreversible CV behaviour shown in Figure 1, the oxidative peaks are most likely due to electrooxidative polymerization of the tested compounds, which proceed through consecutive dimerization steps of electrochemically generated cations leading from a dimer to a tetramer and then finally to a polymer [15].

An important feature in the CV curves of Figure 1 is the potential dependence of the CV peaks on the substituted methyl groups of the benzene ring. With increase in the number of methyl groups, the oxidation peaks for the benzene derivatives are shifted distinctly to

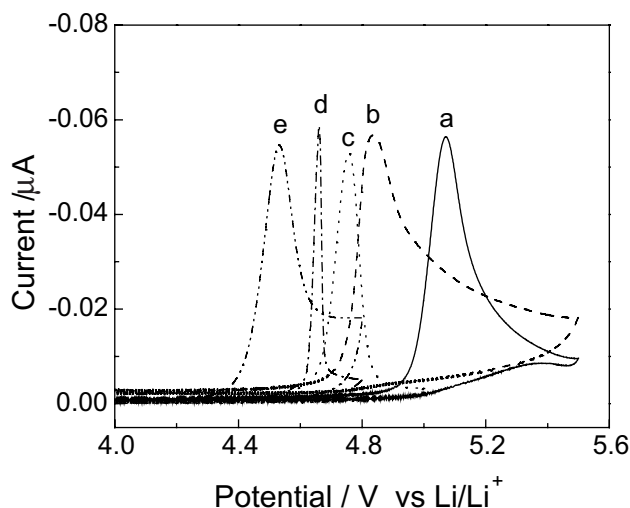


Fig. 1. CV curves of a Pt microelectrode in 1 M LiPF_6/EC + DMC electrolyte containing 5 wt %: (a) benzene, (b) toluene, (c) xylene, (d) 1,2,4-trimethylbenzene and (e) 1,2,4,5-tetramethylbenzene. Scan rate 10 mV s^{-1} .

lower potentials, due to the increase in the p– π conjugation between methyl groups and benzene ring. Thus, it is possible to select a compound with appropriate oxidation potential as a polymerizable additive for shutdown of overcharge reactions at required oxidation potentials.

Among the benzene derivatives tested, xylene seems to be a good candidate for use as a monomer additive because its oxidation peak starts at 4.5 V and reaches a maximum value at 4.75 V (Figure 1), considerably higher than the potential for complete oxidation of the LiCoO_2 cathode (4.3 V) and lower than the decomposition potential of the electrolyte (5.0 V). In addition, the current peak of xylene is sharp indicating fast polymerization kinetics. To ensure the actual feasibility of xylene polymerized on the cathodic oxide materials, the CV experiments were also conducted using a LiCoO_2 powder microelectrode. Figure 2 shows the CV curves obtained

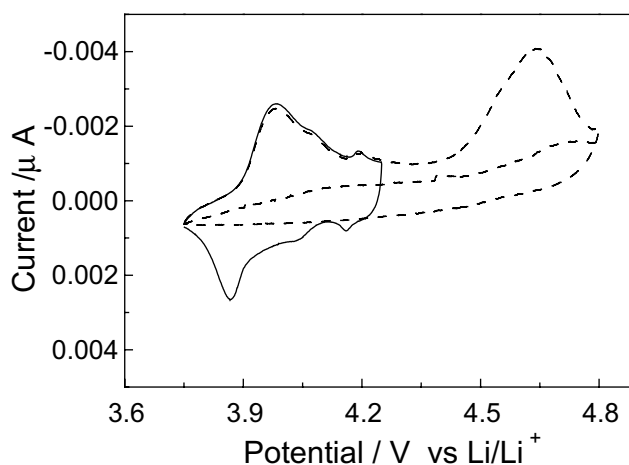


Fig. 2. CV curves of a LiCoO_2 electrode in 1 M LiPF_6/EC + DMC electrolyte containing 5 wt % xylene. Scan rate 1 mV s^{-1} . Sweeping potential region 3.75–4.25 V (solid line), 3.75–4.80 V (dashed line).

from a LiCoO_2 powder microelectrode in the electrolyte containing 5 wt % xylene. It can be seen that when the potential scan is performed below 4.25 V, there are three pairs of reversible oxidation-reduction peaks in the region of +3.75–4.25 V, which is characteristic of the intercalation–deintercalation reactions of Li^+ ion in LiCoO_2 [17]. When the potential is extended to more positive region about +4.8 V, an additional anodic band appears at +4.65 V, indicative of xylene oxidation. In the reverse scan, no cathodic peak corresponding to the reduction of the oxidation product of xylene was found on the cathodic branches of the CV curve. Also, the reversible current peaks due to lithium insertion reactions all disappear in successive scans. These phenomena demonstrate that the xylene additive may not affect the normal lithium insertion reactions at potentials below 4.2 V, but can polymerize at +4.6 V at the LiCoO_2 electrode, leading to a deactivated LiCoO_2 surface for lithium insertion reactions. Since the LiCoO_2 –electrolyte interface is known to be stable up to 4.8 V [2], the oxidative polymerization of xylene at 4.6 V may protect the LiCoO_2 cathode from oxidative decomposition.

3.2. Overcharge behaviours of the polymerizable additives

To further examine the actual overcharge protection behaviour of xylene additive, parallel overcharging tests were also performed on prismatic graphite– LiCoO_2 batteries filled with 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte containing various contents of xylene. The test batteries were firstly cycled at 0.2 C between 2.75 V and 4.20 V three times and then charged at the 1 C rate. Figure 3 shows the changes in voltage of the batteries during prolonged charging. The voltage profiles for the batteries with or without addition of the additive are similar before the completion of normal charging at 4.25 V, implying no significant influence of the additive on the normal charging behaviour. However, when the batteries

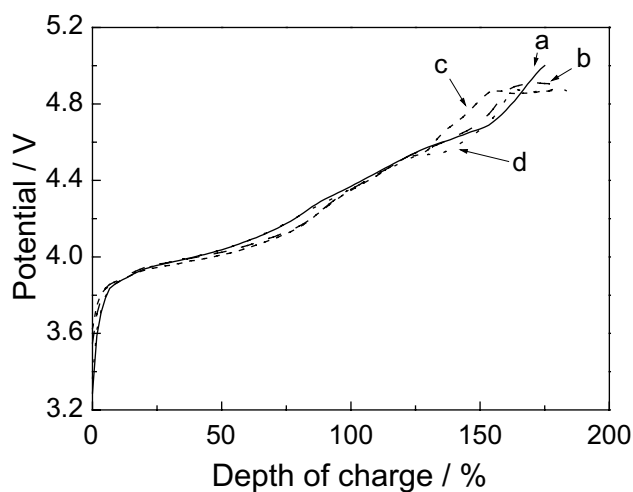


Fig. 3. Charging curves of prismatic C– LiCoO_2 type Li-ion batteries containing: (a) zero, (b) 3 wt %, (c) 5 wt % and (d) 7 wt % xylene. Charging rate 1 C (800 mA).

are subjected to overcharging, the charging curves for the two types of battery are very different. The voltage of the batteries without additive steadily increases to the cut-off voltage (5 V) of the charger, whereas the voltages of the batteries containing xylene stop at about 4.85 V even at prolonged overcharge. Obviously, the voltage plateaus result from oxidation reactions of xylene at the cathodic surface.

It might be argued that a few percent content of xylene in the batteries can only consume a very limited amount of charge which may not be able to provide constant oxidation current as visualized in the charging plateaus at 4.85 V. In previous studies of electrochemical oxidations of benzene derivatives, it is well recognized that the oxidations of benzene derivatives take place through the electropolymerization of benzene rings with release of protons [15, 16]. This mechanism could be used to explain the observed voltage profiles in the presence of xylene. When the charging voltage reaches the oxidation potential, xylene starts to polymerize on the cathode and delivers 2 H^+ for one molecule of xylene. The H^+ ions diffuse to and reduce at the negative electrode to form hydrogen molecules, which can be further oxidized into H^+ ions at the positive electrode. This proton–hydrogen cycling actually acts as a redox couple shuttling between the two electrodes and, therefore, maintains the charging voltage at about 4.85 V.

Figure 4 shows SEM evidence for the polymerization of xylene on the LiCoO_2 electrode. As shown in Figure 4(a), the LiCoO_2 electrode overcharged to 5 V in the absence of xylene exhibits a porous structure with uniform distribution of the electroactive material. However, if the LiCoO_2 electrode was overcharged, even for a short time in the electrolyte containing 5% xylene, the electrode surface appears to be coated with a thin layer of transparent film (Figure 4(b)), due to the electrochemical polymerization of xylene. When the cells were overcharged for a relatively longer time of about 20 min., the LiCoO_2 electrode (Figure 4(c)) showed an entirely blocked surface by the polymerized deposits.

To identify the conductive properties of the deposited surface film, we also monitored the changes in the internal impedances of the batteries during prolonged charging. Figure 5 compares the internal resistance changes of the batteries with and without xylene. For normal charge, both types of battery show slightly lower resistances with increasing depth of charge, apparently due to an increase in the internal temperature of the batteries. When the batteries were charged nearly to their nominal capacities, the internal resistances of the batteries containing the additive increased rapidly at the potential of about 4.6 V, which is in good agreement with the onset potential for the oxidative polymerization of xylene. During overcharge, the resistance of the batteries containing xylene were firstly stabilized at 50 m Ω for a half hour and then climbed suddenly at the end of overcharge. This resistance data may be explained by the fact that at the beginning of overcharge, the rapid increase in the internal resistances



Fig. 4. SEM images of the LiCoO_2 electrode taken from the overcharged cells containing: (a) no additives, (b) 5 wt % xylene, at the beginning of overcharge and (c) 5 wt % xylene, at 100% overcharge.

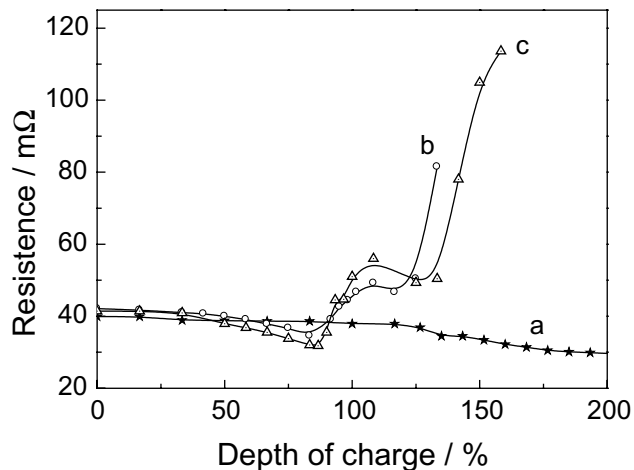


Fig. 5. Changes in the internal resistance of the prismatic C-LiCoO_2 batteries with the depth of charging. Test batteries contain: (a) zero, (b) 3% and (c) 5 wt % xylene.

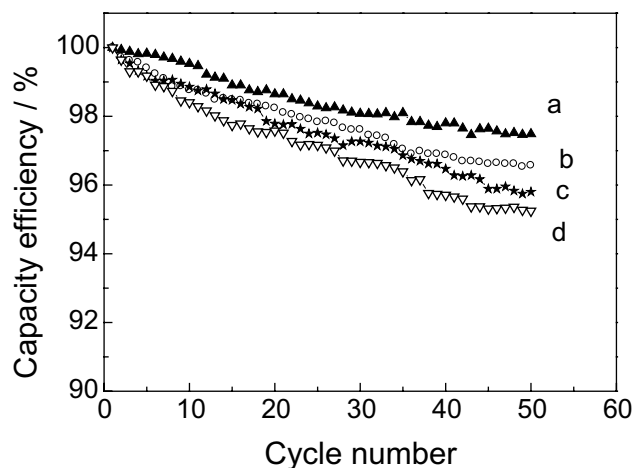


Fig. 6. Cycling properties of the prismatic C-LiCoO_2 batteries containing: (a) zero, (b) 3 wt %, (c) 5 wt % and (d) 7 wt % xylene. Batteries were charged at 1 C rate to 4.2 V followed by potentiostatic charging at terminating current of 20 mA, and then discharged at 1 C rate to 2.75 V for each cycle.

results from the formation of polymer deposits on the cathode and then the observed plateaus in the resistances curves are probably due to the diffusion-controlled polymerization at the middle stage of overcharge. Finally, the sudden rise in internal resistance can be attributed to the full coverage of the electrochemical surface by polymerization products and the swelling of the battery by accumulation gas.

The safety behaviour of the additive for improving the overcharge tolerance of the batteries were also characterized simultaneously. It was found that after only 20 min of overcharging did the skin temperatures of the batteries containing xylene exceed 60°C , and their stainless steel cans severely expanded. Nevertheless, the batteries were very rarely found to burn or explode. In contrast, although the batteries using blank electrolyte exhibited slight changes in skin temperature and in

dimensions at the same depth of overcharge, they were frequently observed to ignite or explode. Since all commercial lithium ion batteries are used with a temperature sensing device and pressure-limiting valve, the rapid responses in the temperature and pressure for batteries with xylene additive may help to enhance the sensitivity of the safety control devices once the batteries are subjected to overcharge, abuse.

3.3. Influences of the additive on normal performance

An electrolyte additive must not only improve overcharge tolerance, but also not affect the normal charge–discharge performance. Figure 6 shows the effects of xylene content on the cycling performance of the prismatic batteries. The results demonstrate that the capacity fading rate only slightly increases with increasing xylene content. For example, the battery free of xylene has a capacity loss of 2.4% after 50 cycles, while the battery containing 7 wt % xylene has a capacity loss of 5% after 50 cycles. In our optimization work, the electrolyte with 5% content of xylene seems to be a good choice for alleviating the capacity fade and overcharge hazards of Li-ion batteries.

4. Conclusions

This study has demonstrated that the electrochemical polymerization of xylene, as an electrolyte additive, can take place at overcharged LiCoO₂ electrodes to produce an isolating polymer film on the cathode surface, resulting in a blocking effect for the oxidation of the cathodic material and electrolyte. This polymerization process can spontaneously release a large amount of heat and gas, causing a rapid increase in the battery temperature and pressure, which help to enhance the sensitivities of the safety devices. In addition, the xylene

additive has shown a slight influence on the cycling behaviour of the Li-ion batteries.

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