



Improvement of high voltage cycling performance and thermal stability of lithium-ion cells by use of a thiophene additive

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ABSTRACT

This study demonstrates that the addition of thiophene improves the cycle life of lithium-ion cells at high voltage. Electrochemical impedance spectroscopy results suggest that addition of thiophene significantly suppresses the increase of the charge transfer resistance that occurs during cycling up to high voltage. Differential scanning calorimetric studies showed that the thermal stability of fully charged LiCoO₂ cathode was also enhanced in the presence of thiophene.

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1. Introduction

Lithium-ion batteries are used as power sources for portable electronic devices and hybrid electric vehicles, due to their high energy density and excellent power capability. To deliver higher reversible capacity, many groups have attempted to develop high voltage cathode materials with high capacity. At high cell voltages, however, the organic solvents used in lithium-ion batteries tend to decompose, leaving a highly resistive surface film on the cathode. This can lead to gradual deterioration of cell performance upon cycling. Numerous possible solutions to this problem have been proposed, such as the development of new electrolytes exhibiting high anodic stability [1–3], addition of various inorganic and organic additives to the electrolyte [4–7], and inorganic coating on the surface of cathode materials [8–10]. Abe et al. investigated several organic additives meant to form a conductive film on the cathode in lithium-ion batteries [7]. The use of organic additives was based on the concept that they could be electrochemically polymerized in the high potential region [11–13].

The objective of the present study is to improve high voltage cycling performance and thermal stability of lithium-ion cells by adding a small amount of thiophene which is capable of being electrochemically polymerized prior to solvent decomposition at high voltages. We evaluated the cycling performance and thermal

stability of the lithium-ion cells assembled with electrolyte containing thiophene. The influences of the charge cut-off potential on cycling performance and thermal stability were investigated in detail.

2. Experimental

2.1. Cell assembly

The electrolyte solution used was 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (3:7 by volume). Thiophene was added at 0.1 wt.% to the electrolyte solution. The cathode was prepared by coating an N-methyl pyrrolidone (NMP)-based slurry containing LiCoO₂, PVdF, and super-P carbon (85:7.5:7.5) onto aluminum foil. Its active mass loading was about 5.0 mg cm⁻². The anode was prepared by coating a NMP-based slurry of mesocarbon microbeads (MCMB), PVdF, and super-P carbon (88:8:4) onto copper foil. The cell composed of a carbon anode, a polyethylene separator (Celgard 2400) and a LiCoO₂ cathode was assembled with an electrolyte containing thiophene in a dry box filled with argon gas. When preparing the cell, 0.5 g of electrolyte solution was added into the cell (geometric electrode area: 30 cm²).

2.2. Measurements

Linear sweep voltammetry (LSV) was performed on a platinum working electrode with lithium counter and reference electrodes at

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a scanning rate of 1.0 mV s^{-1} . AC impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range of 1 MHz – 1 mHz at an amplitude of 10 mV . In order to evaluate cycling performance, the cells were cycled over 3.0 – 4.2 , 3.0 – 4.3 , and 3.0 – 4.4 V at a current rate of 1.0 C . For differential scanning calorimetry (DSC) experiments, the cells were fully recharged to a different cut-off voltage after 100 cycles. After disassembling the cells, the cathode was gently scraped from the current collector. Approximately 5 mg of the cathode was hermetically sealed in a stainless steel pan and measurements were taken at a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$.

3. Results and discussion

From the linear sweep voltammograms performed in the electrolyte solution containing thiophene, two large oxidative current peaks are observed at 4.42 and 4.76 V before solvent decomposition, while the corresponding current peaks are not observed for electrolyte without thiophene. Because thiophene has a higher HOMO (highest occupied molecular orbital) energy than the solvents in the electrolyte solution, it can be easily oxidized at potentials lower than the decomposition potential of the solvent [14]. The first oxidation peak is associated with the oxidation of thiophene monomer or oligomer to its radical cation for electropolymerization and the second one can be ascribed to additional doping reaction [15,16]. The electrochemical oxidation of thiophene results in the formation of a conductive polymer film on the electrode because its polymerization product is electronically conductive in its oxidized state [12,15,17].

The cells with and without thiophene were initially subjected to a preconditioning cycle over different cut-off voltages at 0.1 C rate (Fig. 1). It is seen that both the charge and discharge capacity increase with the charge cut-off voltage. The cells without thiophene show almost the same coulombic efficiency (89.2% , 89.5% , 89.3%), irrespective of the cut-off voltage. However, the coulombic efficiency of the cell with thiophene decreases (89.1% , 88.1% , 85.8%) with increasing charge cut-off voltage. This result may be explained by irreversible electrochemical oxidation of thiophene during the first preconditioning cycle, because the oxidation of thiophene is likely to occur at higher voltage. The oxidative polymerization of thiophene consumes a portion of the capacity which corresponds to irreversible capacity loss.

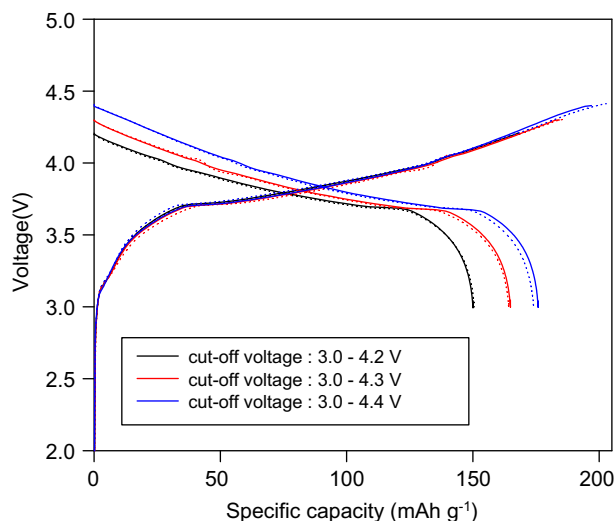


Fig. 1. First preconditioning cycles of lithium-ion cells prepared with liquid electrolyte with (dotted line) and without thiophene (solid line).

After two preconditioning cycles, the cells were cycled over different cut-off voltages at 1.0 C . Fig. 2 shows the discharge capacities of the cells as a function of cycle number. When cells with and without thiophene were cycled between 3.0 and 4.2 or 4.3 V , they exhibited nearly identical cycling characteristics. It can be understood that the formation of a conductive film on Li-CoO_2 cathode may not be sufficient when the cell is charged up to 4.2 or 4.3 V , because thiophene is likely to electrochemically oxidize above 4.3 V vs. Li . On the contrary, the cycling characteristics of the cells were found to depend on the presence of thiophene when they were charged up to 4.4 V . The cell without thiophene showed severe capacity decline with capacity retention of 34.2% after 100 cycles. In this case, electrolyte decomposition occurs and the decomposition products may cover the cathode surface with a highly resistive layer as cycling progresses. On the other hand, the addition of thiophene to the electrolyte solution leads to a remarkably improved cycling stability, which is due to the formation of electronically conductive film on the cathode. The coulombic efficiency of the cell was gradually increased with cycling and maintained to be almost constant after initial few cycles. In the successive charge/discharge cycles, the values are almost same to those in the cell without thiophene. Thus, it is plausible that the growth of conductive film continues to increase up to initial few cycles. From the auger electron spectroscopy depth profile of cathode surface after

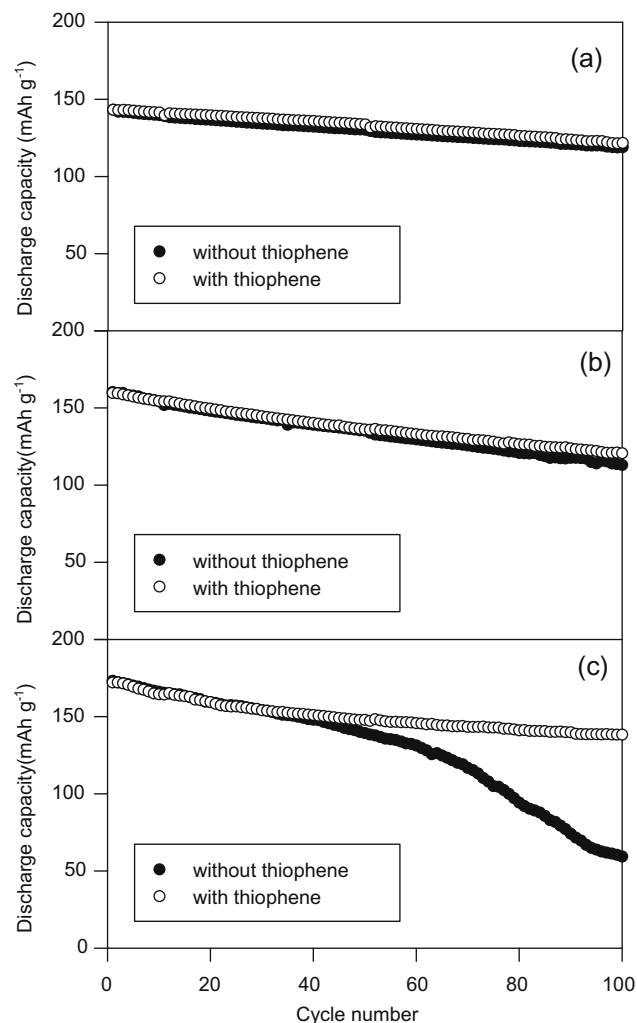


Fig. 2. Discharge capacities of lithium-ion cells as a function of cycle number obtained at different cut-off voltages: (a) 3.0 – 4.2 V , (b) 3.0 – 4.3 V , and (c) 3.0 – 4.4 V .

cycling over 3.0–4.4 V, the film thickness formed on LiCoO_2 was measured to be about 12 nm.

The ac impedance of the cells after the repeated 100 cycles was measured in the fully charged state (Fig. 3). After repeated cycling, two overlapped semicircles were obtained from both cells. According to previous studies of ac impedance [18,19], the semicircle in the high frequency range can be attributed to the resistance due to Li^+ ion migration through the surface film on the electrode and the semicircle in the medium-to-low frequency range is due to charge transfer resistance between the electrode and electrolyte. In cells without thiophene, the charge transfer resistance dramatically increased as the charge cut-off voltage increased from 4.2 to 4.4 V. This result is associated with the growth of a resistive layer on the electrode surface due to electrolyte decomposition at high potential. The resistive layer may hamper charge transport at the electrode and electrolyte interface, which causes the poor capacity retention when cycling up to 4.4 V, as shown in Fig. 2c.

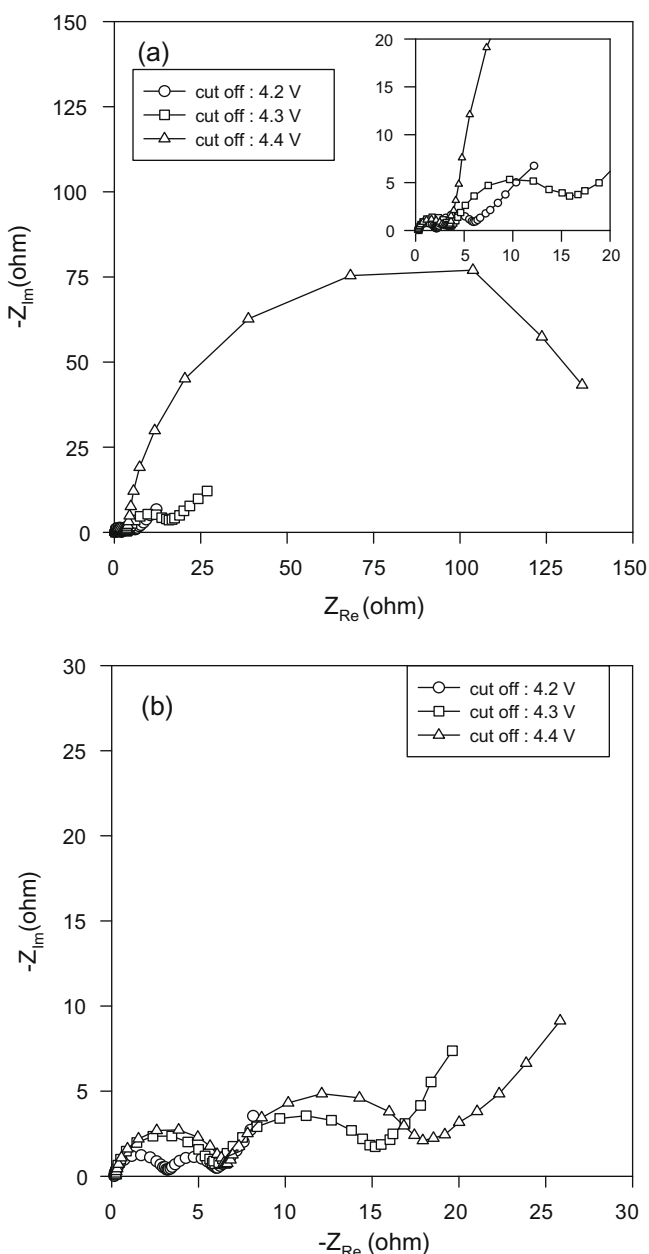


Fig. 3. AC impedance spectra of lithium-ion cells (a) without and (b) with thiophene, which are obtained at the fully charged state after 100 cycles.

On the other hand, interfacial resistance consisting of surface film resistance and charge transfer resistance in the cells with thiophene slightly increased with increasing cut-off voltage. This supports the notion that in the presence of thiophene, a protective conductive film is formed on the cathode at high voltage, which limits the growth of a resistive layer due to electrolyte decomposition.

Fig. 4 shows the DSC profiles of the cathode materials charged to 4.2, 4.3, and 4.4 V. It is clear that the heats of reaction for the LiCoO_2 material in the cell containing thiophene are always lower than those in the cell without thiophene. It should be noted that the reaction heat based on the weight of LiCoO_2 increased from 827.6 to 1,386.0 J g^{-1} with increasing cut-off voltage in the cell without thiophene, but it is decreased from 821.1 to 617.8 J g^{-1} in the cell with thiophene. The first exothermic reaction peak observed in the cell without thiophene is shifted to the low temperature and its reaction heat is increased with cut-off voltage. According to previous reports, the exothermic peak around 200 °C can be ascribed to decomposition of electrolyte caused by active surface of delithiated LiCoO_2 [20,21]. The absence of the peak in the cell with thiophene suggests that the surface reaction is inhibited due to a coating of the electrode particles by thin conductive film, which demonstrates the enhanced thermal stability of the cathode material in the presence of thiophene. These DSC results suggest that the conductive polymer layer formed on LiCoO_2 in the high voltage region renders the cathode material less reactive towards the liquid electrolyte, leading to an improvement of thermal stability. Further evaluation of thiophene as a high voltage additive for 5 V class high voltage lithium-ion cells is currently under investigation by our group.

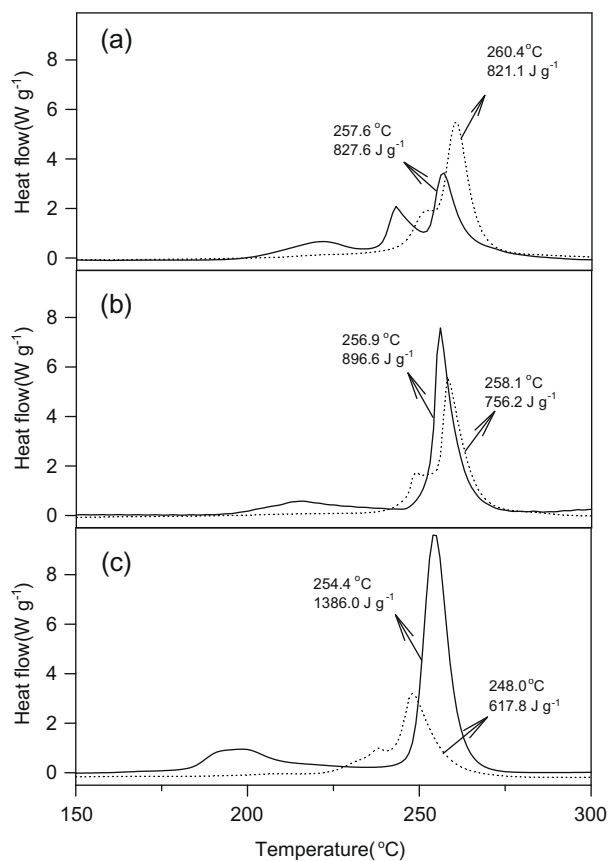


Fig. 4. DSC profiles of LiCoO_2 cathode material charged to (a) 4.2 V, (b) 4.3 V, and (c) 4.4 V, which contains liquid electrolyte with (dotted line) and without thiophene (solid line).

4. Conclusions

We demonstrated that the oxidative decomposition of electrolytes at high voltage could be suppressed by adding a small amount of thiophene. Lithium-ion cell containing thiophene exhibited a high initial discharge capacity of 174.1 mAh g⁻¹ in the voltage range of 3.0–4.4 V and its capacity retention and thermal stability were greatly improved. Good capacity retention at high cut-off voltages could be ascribed to the formation of a conducting film which suppresses electrolyte decomposition on cathode.

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