

# Improvement in High-voltage Performance of Lithium-ion Batteries Using Bismaleimide as an Electrolyte Additive



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## ABSTRACT

N,N'-4,4'-diphenylmethane-bismaleimide (BMI) is attempted to enhance the high-voltage performance for lithium-ion batteries. When 0.1% (m/v) BMI is added into the control electrolyte, the high-voltage cycling performance of LiCoO<sub>2</sub>/Li cells is improved evidently while charging the cell up to 4.5 V rather than the conventional 4.2 V. Analysis of scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) demonstrate that an interface film forms on the cathode surface from BMI in electrolyte. AC impedance spectra and charge/discharge test were tested after incubation of the charged cell at 60 °C. Linear sweep voltammetry (LSV) is used to test the electrochemical stability window of the electrolyte with BMI addition. The results demonstrate that the improvement of high-voltage performance is attributed to the surface film on cathode. In addition, the BMI addition does not cause damage in conventional performance with 4.2 V electrochemical window. The BMI-containing electrolyte provides high-voltage cycling performance with 4.5 V electrochemical window, making LiCoO<sub>2</sub> battery a simple and promising system for applications with high energy density.

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## 1. Introduction

Improving energy density is one of the biggest challenges for lithium-ion batteries while meet the new markets such as smart mobile devices, electric vehicles and energy storage systems. [1–4] Increasing the charging cut-off voltage has been proposed as an effective approach to improve the energy density of the corresponding batteries. [5–8] However, high voltage always lead to harmful interphasial side reactions between cathode and liquid electrolyte, then lead to resistance increase, and finally seriously pose the capacity decrease and cycle performance deterioration. [9,10] In today's market, the majority of lithium-ion batteries using organic carbonate esters as electrolyte solvents usually takes 4.2 V as the upper charging voltage limit. [6,11]

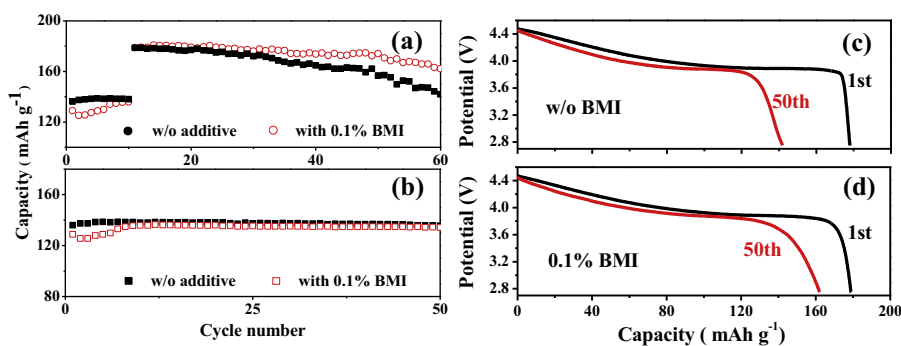
At present, there are two effective methods to solve this problem. Firstly, cathode surface coating with metal oxides, such as Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, MgO, and ZnO, has been used to suppress the interphasial instability between cathode and liquid electrolyte. [12–16] However, these inorganic coatings always form an energy

barrier and hinder lithium ion transfer between the electrode and electrolyte; thereby decrease the C-rate capacities of the cathodes. Secondly, electrolyte additives provide an effective method to improve the interphasial stability between cathode and electrolyte. Recently, a branched bismaleimide oligomer (also known as STOBA) was utilized as an electrolyte additive for lithium ion batteries. It was reported that the oligomer additive can decrease the irreversibility of electrochemical reactions by decreasing the cell polarization from the electrode surface. [17,18] The bismaleimide monomers from which the STOBA is polymerized as electrolyte additive was also researched. Wang et al. [19] reported that the maleimide-based molecules as additive in electrolyte could form uniform and stable surface electrolyte interface (SEI) on meso-carbon microbeads (MCMB), and then improve the cycle capacity retention by reducing the severity of irreversible phenomena during the cycle process. However, bismaleimide used to improve the cathode performance, especially the high-voltage performance, has not been fully studied yet.

In this study, a bismaleimide monomer, N,N'-4,4'-diphenylmethane-bismaleimide (BMI), is studied as an additive in electrolyte for lithium ion batteries. LiCoO<sub>2</sub> is chosen as the model cathode. An attempt is made herein to increase the high-voltage cycling performance by tailoring a stable cathode surface using electrolyte additive. In this short communication, we report firstly

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**Fig. 1.** Discharge capacities (charge/discharge current density = 0.2 C/0.2 C) as a function of cycle number for cells with and without BMI addition (concentration = 0.1% w/v) at room temperature: (a) under a voltage range of 2.75 to 4.5 V (after 10 cycles under a voltage range of 2.75 to 4.2 V); (b) under a voltage range of 2.75 to 4.2 V. Comparison of discharge profiles (1st and 50th) of cells at charge/discharge current density of 0.2 C/0.2 C under a voltage range of 2.75 to 4.5 V: (c) without additive; (d) with BMI addition.

the encouraging results that obtained from the BMI additive which could apparently improve the high-voltage cycling performance, without weaken other electrochemical performances, such as C-rate discharge capacities, et al.

## 2. Experimental

1 M LiPF<sub>6</sub> in EC/DEC (1:1, m/m) supplied by Capchem Co, Ltd. was selected as the base electrolyte (control). The experimental electrolyte was prepared by adding proper amount of BMI into the base electrolyte to make its concentration 0.1% (w/v). LiCoO<sub>2</sub> cathodes consisted of 85 wt.% LiCoO<sub>2</sub>, 5 wt.% SP, 5 wt.% KS and 5 wt.% polyvinylidene difluoride (PVDF). A coin cell (type 2032) was assembled by sandwiching a PP-PE-PP composite separator (thickness = 25 μm, Celgard) between a lithium foil anode and the LiCoO<sub>2</sub> cathode. The unit cells were then activated by being filled with the above electrolytes.

The electrochemical performance of the LiCoO<sub>2</sub>/Li cells, such as discharge capacity, cycleability and C-rate capacity et al., was examined using battery test equipment (LAND). The cyclability of the cells was conducted at a constant charge/discharge current density of 0.2 C/0.2 C in the potential range of 2.75–4.2 V or 2.75–4.5 V at room temperature (25 °C). The C-rate capabilities were evaluated by varying the discharge current densities (i.e., discharge C-rates) from 0.2 C to 10.0 C at a constant charge current density of 0.2 C under a voltage range of 2.75 to 4.2 V.

The incubating experiment was conducted after charging the cell to 4.5 V (0.2 C constant current to constant voltage). The cells with and without BMI addition were left into an incubator maintained at 60 ± 0.5 °C for one and two weeks respectively. The AC impedance spectra of the cells were measured before and after incubation using a Zahner electrochemical workstation (model IM6ex) over a frequency range of 10<sup>-2</sup> to 10<sup>-6</sup> Hz. 0.2 C and 1.0 C discharge capacities of the cells (at a constant charge current of 0.2 C) were tested after incubating for one week.

The electrochemical stability of the electrolyte was determined by LSV on the electrochemical workstation with a scanning rate of 1.0 mV s<sup>-1</sup> from 3.0 to 6.0 V at room temperature, using stainless steel as the working electrode and lithium foil as both the counter and the reference electrode.

The cathode plates were removed from LiCoO<sub>2</sub>/Li coin cells after 10 cycles at charge/discharge current density of 0.2 C/0.2 C under a potential range of 2.75 to 4.2 V. Then, the cathode plates were washed with propylenecarbonate (PC) for three times and dried in a vacuum chamber for SEM (JSM7001F) and XPS (ESCALAB 250XI) tests.

AC impedance measurements were conducted under LiCoO<sub>2</sub>/Li coin cells at room temperature using the electrochemical

workstation. The frequency range and voltage amplitude were set from 100 kHz to 0.02 Hz and at 5 mV, respectively.

## 3. Results and discussion

The effect of BMI additive on the high-voltage cycling performance of LiCoO<sub>2</sub>/Li cells was investigated. Fig. 1 shows the capacity retention during the first 50 cycles of cells at a constant charge/discharge current density of 0.2 C/0.2 C in the potential range of 2.75–4.5 V (after 10 cycles in the potential range of 2.75–4.2 V) and 2.75–4.2 V, respectively. As shown in Fig. 1a, the cycle performance between 2.75 and 4.5 V is significantly better with BMI-containing electrolyte than that of the control electrolyte after the first 20 cycles. The discharge profiles (the 1st and 50th cycle) of the cells with and without BMI addition are also provided in Fig. 1c and 1d. In the beginning of cycling, there is little difference in the discharge capacities between the cells with and without BMI addition. However, as the cycle number increases (more specifically, after the 20th cycle), the control cell suffers from the severe fading of capacity, resulting in a low discharge capacity. The cell with BMI-containing electrolyte show discharge capacity of 162 mAh g<sup>-1</sup> after 50 cycles, and the control experiment is only 142 mAh g<sup>-1</sup>. In addition, under the potential range of 2.75 to 4.2 V, the BMI containing cell also provides excellent discharge capacities up to 50 cycles, which appears to be comparable to the cycleability of the control experiment except the first 10 cycles during which there appears a capacity decrease in the BMI-containing cell (Fig. 1b). Besides, we found that the first 10 cycles is crucial for the later high-voltage cycleability, because the high-voltage performance of cells with BMI in electrolyte have no difference with that of cells without additive, when the batteries directly cycled at charging cut-off voltage of 4.5 V (Fig. 2).

Generally speaking, high-voltage cycling performance is mainly attributed to three factors: cathode structure, cathode/electrolyte interphasial property and electrolyte stability. In this study, we presume that the property of the interphasial film between cathode and electrolyte is the major factor to the cell cycle performance under high voltage. [7,8] So, we try to find by SEM what happened on the surface morphology of the LiCoO<sub>2</sub> cathode. Fig. 3 shows the cathode surface morphology. From Fig. 3a (without additive) and 3b (with BMI addition), It can be seen that the LiCoO<sub>2</sub> particle surface of that with BMI addition is much rougher compared to that of the control experiment, and a film appears to be coated on its surface. Similarly, this rough film can be seen obviously from the images which focus on the flake graphite (Fig. 3c and d). Flake graphite in Fig. 3d (with BMI addition) shows relatively rough surface and fuzzy edges, rather than smooth surface and clear edges of the flake graphite in Fig. 3c (without additive). Evidently, a new film was generated on the cathode surface in the BMI-containing cell.

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