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Thiophene derivatives as novel functional additives for high-voltage $LiCoO_2$ operations in lithium ion batteries

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ABSTRACT

Thiophene derivatives (THs) are examined as novel functional additives for improving the cycling performance of high-voltage $LiCoO_2$. Our investigation reveals that 2,2′-Bithiophene (2TH) and 2,2′:5′,2″-Terthiophene (3TH) can be electrochemically polymerize prior to the electrolyte solvent decomposition to form a protective layer of conducting polymer film on the cathode surface, which blocks off severe electrolyte decomposition at high voltages and, therefore, improves the cycling stability of high voltage $LiCoO_2$ cathode. After 100 cycles at a high cutoff voltage of 4.4 V, the discharge capacity retention is 50% in the base electrolyte, in contrast, the $LiCoO_2$ cathode cycled in the electrolyte containing 0.1 wt% 3TH displays a high capacity retention of 84.8% at 0.25 C rate. This work demonstrates that these thiophene derivatives have considerable potential as functional additives for the applications in high-voltage lithium-ion batteries.

1. Introduction

Lithium cobalt oxide ($LiCoO_2$), with a practical capacity of 120~130 mAh g^{-1} in the operation potential range between 2.7 and 4.2 V (vs. Li^+/Li), has been widely used as the positive material for commercialized lithium ion batteries (LIBs) since its discovery in 1991 [1]. Charging the $LiCoO_2$ above 4.2 V is proposed to be beneficial for its reversible capacity. However, overcharging $LiCoO_2$ can accelerate the oxidation of the electrolyte at higher potentials, result in the formation of a high impedance film on the $LiCoO_2$ surface, and correspondingly lead to a severe deterioration of the cycling performance [2–6].

To suppress the standard liquid electrolyte decomposition at higher voltages on the $LiCoO_2$ electrode, researchers have adopted various strategies to enhance the electrochemical performance of $LiCoO_2$ cathodes at a high-voltage. Previous studies have demonstrated that the electrolyte decomposition can be effectively depressed in surface decoration by depositing various metal oxides such as Al_2O_3 [7], ZnO [8], $AlPO_4$ [9] and SnO_2 [10]. However, because of material modification through complicated chemical synthetic procedures, which are difficult to extend for large-scale battery applications. According to recent reports, the formation of protective films through the use of reducible and oxidative additives in the electrolytes is thought to be one of the most effective and easiest strategies to stabilize the electrode-electrolyte interface. To alleviate the oxidative decomposition of electrolytes, the effect of low concentrations of Methylene methanedisulfonate (MMDS) [11], tris(trimethylsilyl) phosphate (TMSP) [12] and 5-hydroxy-1H-indazole (HI) [13] has been explored. Unfortunately, there are still only few electrolyte additives reported for the high voltage operation of $LiCoO_2$. A few years ago, Abe et al. reported several organic additives meant to form a conductive film on the cathode in lithium-ion batteries [14]. The results show that these additives tend to be electrochemically polymerized more quickly than the base electrolyte solution during charging cells, and form a conductive film on the $LiCoO_2$ cathode, and then suppress the decomposition of electrolyte solvents [15,16]. Although these additives can electrochemically oxidize on the $LiCoO_2$ cathode surface at high voltages, and improve the cycling performance of the cells. However, they are likely to electrochemically polymerize above 4.4 V vs. Li^+/Li (for example, thiophene (TH) and biphenyl (BP), their oxidation potentials are 4.42 and 4.54 V vs. Li^+/Li respectively), which may result that the formation of a conductive film on the $LiCoO_2$ cathode may not be sufficient when the cell is charged up to 4.4 V.

For this reason, we chose the oligomers of thiophene including 2,2′-Bithiophene (2TH), and 2,2′:5′,2″-Terthiophene (3TH) as functional additives to suppress electrolyte decomposition during $LiCoO_2$ cycling stability at high voltage operation. As we all known, the oligomers of thiophene (2TH and 3TH) can be easily oxidized at potentials lower than that of thiophene monomer (TH). Fig. 1 illustrates the working mechanism of surface on the cathode at

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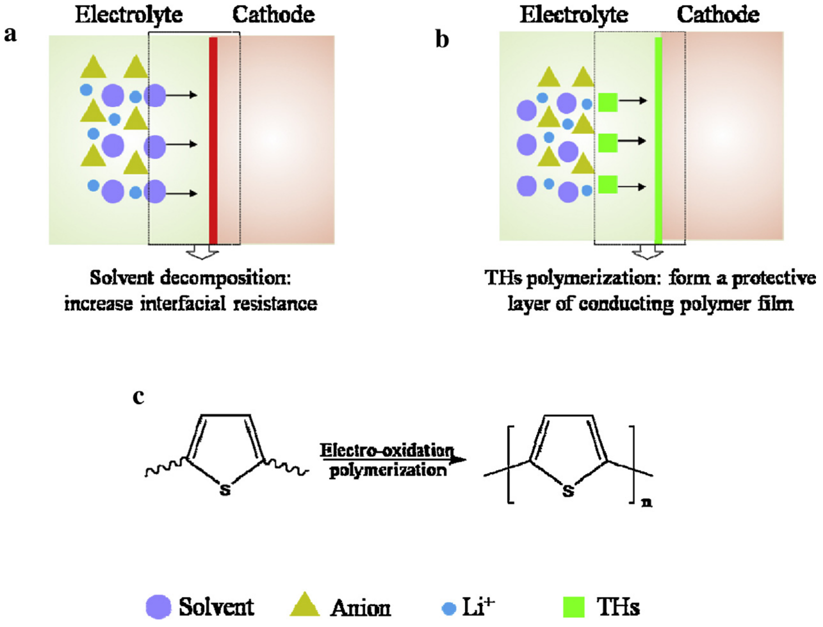

Fig. 1. Schematic models of surface on the cathode at high potentials in liquid electrolytes without additive (a) and with THs additives (b); (c) the electrochemical polymerization reaction of THs additives at 1st charged.

high potentials in liquid electrolytes without additive and with THs additives. As displayed in Fig. 1a, electrolyte solvents without additive suffer from the severe oxidative decomposition beyond the upper voltage limit of $LiPF_6$-based conventional electrolyte, around 4.3 V vs. Li^+/Li. This leads to the formation of a resistive and unstable surface film consisting of inorganic lithium salts and organic carbonates in the cathode. As a result, large irreversible capacity is observed for the $LiCoO_2$ cathode with conventional electrolytes. Selection of thiophene derivatives (THs) as functional additives in this study is mainly based on the consideration that THs can be electrochemically polymerize prior to the electrolyte solvent decomposition to form a protective layer of conducting polymer film on the cathode surface, which blocks off the decomposition of both the solvent and salt in electrolyte at high voltages and, therefore, improves the cycling stability of high voltage $LiCoO_2$ cathode. Furthermore, polythiophene derived from the electrochemical oxidative polymerization of thiophenes has usually high conductivity [17], excellent chemical stability [18,19], and easily forms a homogeneous and compact coating layer on the surface of $LiCoO_2$, and therefore effectively improve the cycling stability of high voltage $LiCoO_2$ cathode.

In this paper, we presented thiophene (TH), 2,2′-Bithiophene (2TH), and 2,2′:5′,2′′-Terthiophene (3TH) as functional additives with the aim of modifying the SEI film to suppress electrolyte decomposition during $LiCoO_2$ cycling stability at high voltage operation. Fig. 2 showed the structures of these molecules. As shown in Fig. 2, the difference between TH, 2TH and 3TH is the number of the thiophene unit. First, we examined the effect of thiophene-unit number on the anodic stability of these additives itself through both Density functional calculations (DFT) and Linear sweep voltammograms (LSV). Then, the performance of the additives were investigated for $LiCoO_2$ electrode at high voltage operation via combination of battery performance test and Electrochemical impedance spectroscopy (EIS), as well as Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) measurements.

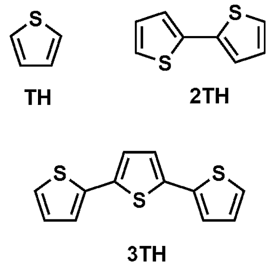

Fig. 2. Chemical structures of thiophene (TH), 2,2′-Bithiophene (2TH), and 2,2′:5′,2′′-Terthiophene (3TH).

2. Experimental

2.1. DFT calculations

The Kohn-Sham DFT equation was calculated with the B3PW91 functional [20,21] and 6–311 + +G (d, p) basis sets of diffuse-augmented triple-ζ quality. The ground-state structures of the molecules were fully optimized within C1 symmetry by means of DFT methods. All the DFT calculations were performed using the Gaussian 09 program package [22].

2.2. Chemicals

Reagent grade thiophene (TH), 2,2′-Bithiophene (2TH), and 2,2′:5′,2′′-Terthiophene (3TH) were purchased from J & K Scientific Ltd. These electrolyte additives were used as received without further purification. The electrolyte solution was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), and dimethyl carbonate (DMC) (3:7 by Vol.), purchased from Guotai-Huarong New Chemical Materials Co., Ltd. (Zhangjiagang, China). The $LiCoO_2$ was obtained from Ningbo Veken Battery Co., Ltd. (Ningbo, China).

2.3. Electrochemical measurements

To estimate the oxidation potential of the electrolytes, the linear sweep voltammetry experiments using an Autolab Electrochemical Analytical Instrument (ECO CHEMIE, B. V. Utrecht, The Netherlands) were measured in three-electrode electrochemical cell with a Pt disk of 0.1 mm diameter as working electrode, Li foil