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Improving high voltage stability of lithium cobalt oxide/graphite battery via forming protective films simultaneously on anode and cathode by using electrolyte additive

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ABSTRACT

We report a new finding that high voltage stability of lithium cobalt oxide ($LiCoO_2$)/graphite battery can be improved by using vinyl ethylene carbonate (VEC) as an electrolyte additive. Charge/discharge tests demonstrate that the battery using VEC exhibits significantly improved cyclic and dimensional stability of the 053048-type $LiCoO_2$/graphite pouch cell up to 4.5 V. The capacity retention is 87.0% and the swell value in thickness is 3.1% for the cell with 2.0 wt.% VEC after 400 cycles between 3.0 V and 4.5 V, compared to the values of 38.4% and 38.6%, respectively, for the cell without additive. The characterizations from scanning electron spectroscopy and X-ray photoelectron spectroscopy demonstrate that VEC facilitates the formation of stable solid electrolyte interfaces simultaneously on anode and cathode of the $LiCoO_2$/graphite battery, yielding effective protections for anode and cathode and preventions of the electrolyte decomposition on both electrodes.

1. Introduction

Lithium ion batteries are presently one of the major power sources for portable electronic devices, and expected to be the main power sources for electric vehicle [1]. Among various cathode materials, lithium cobalt oxide ($LiCoO_2$) is still the most widely used for commercial lithium ion batteries due to its easy preparation, excellent cycling performance, and reasonable rate capability. However, its practical capacity is limited to half of its theoretical value (274 mAh/g) in order to maintain a reasonable cycling stability [2,3]. Increasing the operation voltage to more than 4.2 V (vs. Li^+/Li) yields both higher operating voltage and larger capacity of $LiCoO_2$ and thus improves significantly the energy density of the cell. Unfortunately, the charging over 4.2 V (vs. Li^+/Li) is accompanied by the microcracks within the particles [4,5], the cobalt dissolution from $LiCoO_2$ and the decomposition of electrolyte [6–8]. The dissolved cobalt subsequently moves toward anode and deposits on anode graphite surface [9], which does not facilitate the formation of a protective solid electrolyte interface (SEI) on the graphite anode. Consequently, a noticeable capacity loss is usually observed in $LiCoO_2$/graphite batteries at high operating voltage.

It has been reported that surface modification of $LiCoO_2$ with coating materials, such as Al_2O_3 [10], ZrO_2 [11], ZnO [12], Li_3PO_4 [13], and $AlPO_4$ [14], can improve its cycle performance at higher voltage. However, the surface coating is usually at the cost of capacity loss and increases the manufacturing cost.

Graphite is currently the most used anodic material in lithium ion batteries due to its high capacity and good cycling stability [15–18]. Since the layered structure of graphite for lithium insertion is easily destroyed by the irreversible reactions of electrolyte on anode, additives are necessary to form a SEI film to protect graphite and prevent electrolyte decomposition [19–22]. Recently, the idea for the protection of graphite anode by SEI was adopted for the protection of cathodes and the prevention of electrolyte decomposition on the cathode [23–25].

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Several additives have been proposed for the formation of a protective SEI film on $LiCoO_2$ cathode and the improvement of high voltage stability of $LiCoO_2$-based batteries [26–32]. Among these additives, vinylene carbonate (VC), a well-known SEI-forming additive for graphite anode, is most attractive. The improved cycling performance of $LiCoO_2$-based batteries at high cutoff voltage by VC is attributed to not only the stable SEI formed by VC on graphite anode [7,31], but also the polymer film formed from the oxidation of VC on $LiCoO_2$ cathode, which protects the cathode and prevents the electrolyte decomposition [32]. However, the formation of anodic SEI and cathodic films by VC is accompanied by the evolution of CO_2 [7,24,33–35].

Compared to VC, vinyl ethylene carbonate (VEC) is more stable and has thus attracted much attention in recent years [36–39]. Due to its electron-rich double bond and can be reduced at potentials above 1.0 V (vs Li^+/Li), VEC shows its ability to improve battery performance as an effective film-forming additive for graphite anode, especially in propylene carbonate based electrolytes [36]. Interestingly, VEC was also found to be able to form protective film on $LiNi_{0.8}Co_{0.2}O_2$ cathode and to improve battery performance at elevated temperature (50 °C) [40].

With this knowledge, we made an attempt to use VEC as an electrolyte additive to improve the high voltage stability of $LiCoO_2$/graphite battery. It was found that VEC can form protective SEI films simultaneously on graphite anode and $LiCoO_2$ cathode and thus improve significantly cycling stability of $LiCoO_2$/graphite battery up to 4.5 V.

2. Experimental

$LiCoO_2$ electrode was prepared by coating an aluminum foil current collector with a slurry of 94.0 wt.% $LiCoO_2$ (Hunan Reshine New Material Co., Ltd), 3.0 wt.% conductive carbon, and 3.0 wt.% polyvinylidene fluoride (PVdF). Graphite electrode consisted of a mixture of 95.0 wt.% graphite (BTR Battery Materials Co., Ltd), 1.0 wt.% Super-P, 1.5 wt.% carboxymethyl cellulose (CMC) and 2.5 wt.% styrene butadiene rubber (SBR). 2025-type coin cells of $LiCoO_2$/Li were set up in a glove box (Mbraun Unilab MB20) with microporous membrane (Celgard 2400) separators. Each coin cell contained 30 μL of electrolyte. 053048-type pouch full-cells were fabricated with $LiCoO_2$ electrode as cathode, microporous membrane (Celgard 2400) as separator and graphite electrode anode. To make the best use of cathode capacity, the graphite was designed to be excess with a capacity ratio of anode/cathode being 1.1. The capacity is defined as 340 mAh/g for graphite anode and 180 mAh/g for $LiCoO_2$ cathode.

Battery grade solvents, ethylene carbonate (EC) and ethyl methyl carbonate (EMC), were provided by Guangzhou Tinci Materials Technology Co. Ltd., China. Lithium hexafluorophosphate ($LiPF_6$, battery grade) was purchased from Hashimoto Chemical Corporation. Vinyl ethylene carbonate (VEC, >99%) was purchased from Aladdin. All these chemicals were used without further purification. The base electrolyte in this work was 1.0 M $LiPF_6$/EC-EMC (1:2 by weight). The cell assembling and electrolyte preparation were conducted in the glove box (Mbraun Unilab MB20) under a dry argon atmosphere (the content of water and oxygen was controlled to lower than 0.1 ppm).

$LiCoO_2$/Li cells were cycled at 0.2 C rate on a LAND cell test system (Land CT 2001A). Linear sweep voltammetry was performed on Solartron-1480 (England) in the potential range of 3.0-4.5 V (vs. Li^+/Li) at a scanning rate of 0.1 mV/s. The charge/discharge behaviors of the pouch full-cells were tested using a computer controlled battery charger test (BS-9300R, Qingtian, Guangzhou) at 1 C in the range of 3.0-4.2 V and 3.0-4.5 V. Five cells were tested with each electrolyte and the reported charge/discharge results are the average values of top three cells. The full cell performance was described with capacity and energy densities based on the weight of $LiCoO_2$ in kilogram. The energy density was obtained by:

$$\text{Energy density (Wh/kg)} = \text{C (Ah/kg)} \times \text{E (V)}$$

where C and E were the discharge capacity density of the cell based on the weight of $LiCoO_2$ and the voltage of the cell at half discharge capacity, respectively. The obtained voltage is 3.7 V for 4.2 V end-off cell and 3.9 V for 4.5 V end-off cell. The thickness of the cells was measured with a vernier caliper and the swell value of the cycled cells was calculated by:

$$\text{Swell value (\%)} = \frac{(T - T_0)}{T_0} \times 100$$

where T_0 and T were the thickness of the cell before and after cycling at the range of 3.0-4.5 V, respectively.

The cycled graphite and $LiCoO_2$ electrodes for structure and composition characterizations were washed three times with dimethyl carbonate to remove $LiPF_6$ precipitated on the electrodes, and then evacuated overnight at room temperature. The morphology was observed by scanning electron microscopy (SEM) and the element contents were analyzed with energy dispersive X-ray spectroscopy (EDS) on a JEOL-5900 SEM. Thermal behaviors were analyzed on Perkin-Elmer TGA7 from room temperature to 600 °C. The X-ray photoelectron spectroscopy (XPS) spectra were obtained on ESCALAB 250 using a focused monochromatized Al K_α radiation ($h\upsilon$ =1486.6 eV) under ultra high vacuum, while final adjustment of the energy scale was made based on the C 1s peak of graphite at 284.3 eV. The spectra obtained were fitted using XPSPeak 4.1. Lorentzian and Gaussian functions were used for the least-square curve fitting procedure.

3. Results and discussion

The effects of VEC on the charge/discharge performance of $LiCoO_2$ cathode was evaluated on $LiCoO_2$/Li half cells. The obtained results are presented in Fig. 1. As shown in Fig. 1A, the cell with base electrolyte exhibits good cycling stability when it is cycled in the voltage range of 3.0-4.2 V (vs. Li^+/Li), suggesting that $LiCoO_2$/electrolyte system is stable, i.e., $LiCoO_2$ does not suffer destruction and electrolyte does not decompose. The similar cycling performance for the cells with and without VEC indicates that VEC does not yield negative effect on the cathode.

However, when cycled in the voltage range of 3.0-4.5 V (vs. Li^+/Li), the cell without VEC shows a significant capacity drop, from 181 mAh/g to 131 mAh/g, with a capacity retention of 72.4% after 20 cycles. The poor cycling stability of $LiCoO_2$ cathode should

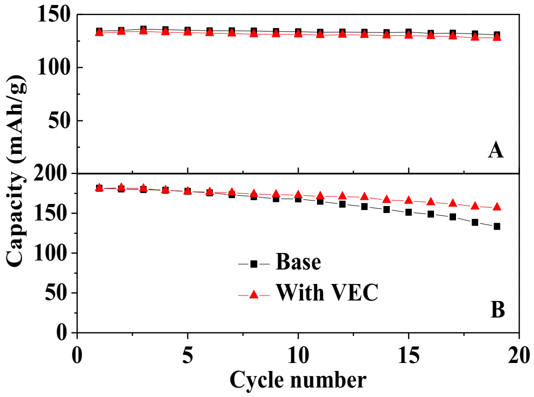

Fig. 1. Charge/discharge performances of the $LiCoO_2$/Li cells in 1.0 M $LiPF_6$/EC-EMC (1:2) without additive and with 1.0 wt.% VEC in voltage range of 3.0-4.2 V (vs. Li^+/Li) (A) and 3.0-4.5 V (vs. Li^+/Li) (B).