Improved compatibility of graphite anode for lithium ion battery using sulfuric esters

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ABSTRACT

Ethylene sulfate (DTD), propylene sulfite (1,2-PS) and trimethylene sulfate (1,3-PCS) were investigated as electrolyte additives in lithium ion battery. Density functional theory (DFT) calculation shows that DTD, 1,2-PS and 1,3-PCS possess relatively low lowest unoccupied molecule orbital (LUMO) energies, which is easier to be reduced on the graphite anode. The CV curves, cycling performance and AC impedance of Li/graphite half cells reveal that DTD and 1,3-PCS were preferentially reduced to form stable SEI films. The initial efficiency, cycling performance and high temperature storage properties were greatly improved in the electrochemical tests by adding 1% DTD to $LiCoO_2$/graphite battery. The SEM images show that the graphite electrode surface with SEI film formed by adding 1% DTD became smoother and more homogeneous. IR analysis results show that the SEI film included both inorganic components (Li_2SO_3 and Li_2CO_3) and organic components ($ROCO_2Li$ and $ROSO_2Li$).

1. Introduction

Since the introduction of lithium ion batteries (LIBs) in electronic products, driving power, and energy storage fields, the researches on related electrode materials have been rapidly developed. At present, the commercial anode and cathode materials are continued to mature. Electrolyte becomes the key component to constrain the electrochemical performance of LIBs. Commercial anode electrode material is mainly natural graphite in rechargeable LIBs. Artificial graphite (AG) with high-specific capacity and high compaction density is popular recently. However, the compatibility between AG and electrolyte restricts the battery's overall performance, and becomes a key point for researchers in improving the electrochemical performance of LIBs. During the first cycle of LIBs, a passivation surface film named as solid electrolyte interface (SEI) appears on the graphite electrode surface. This effective SEI film offers good compatibility between graphite and electrolyte. Usually, the compatibility is improved by changing solvent composition, adding additive and lithium salt.

In recent years, electrolyte additives containing sulfur have been paid a lot of attention to improve the properties of SEI film [1–4]. SO_2 is the earliest sulfuric additive, which can change the morphology of SEI film effectively [5,6]. However, it is not in widespread use because of its low solubility and increased interior pressure. Wrodnigg G H [7,8] reported that ethylene sulfite (ES) and propylene sulfite (1,2-PS) could improve the electrochemical stability of the $LiMn_2O_4$ cathode. Yu [9] also suggested that ES could significantly improve the performance of $LiCoO_2$/graphite battery. In our work, we found that ethylene sulfate (DTD) and trimethylene sulfate (1,3-PCS) have similar structures with ES and 1,2-PS. In addition, DTD, 1,2-PS and 1,3-PCS have lower lowest unoccupied molecule orbital (LUMO) energies, resulting in that they are easier to be reduced to form SEI film on the graphite anode. AG with compacted density of 1.65 $g \cdot cm^{-3}$ and specific capacity of 340 $mAh \cdot g^{-1}$ is employed to investigate the electrochemical performance of LIBs with these additives.

2. Experimental

2.1. Materials and electrode preparations

Lithium hexafluorophosphate ($LiPF_6$) and organic solvents such as ethylene carbonate (EC), ethyl methyl carbonate (EMC) and

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dimethyl carbonate (DMC) were provided by Jiangxi Youli New Materials Co. Ltd., China. The electrolytes of $1 \, mol \, L^{-1}$ $LiPF_6$/ EC + DMC + EMC(1:1:1) were used as the blank electrolyte (BE). The additives of DTD, 1,2-PS, and 1,3-PCS were provided by Fujian Chuangxin Science and Technology Develops Co., Ltd., China, and they were added with the amount of 1% (refers to weight percentage) into BE, respectively. Preliminary experiments had shown that the amount of 1% additive was sufficient to improve the electrochemical performance of LIBs. All these chemicals were used without further purification.

AG was provided by Shanghai Shanshan Super Energy Composite Materials Co., Ltd., China, which possesses a good graphitization degree structure determined by X-ray diffraction (XRD, CuKα radiation, Rint-2000, Rigaku). The graphite electrode was prepared with 90% AG, 3% acetylene black, and 7% polyvinylidene fluoride (PVDF), coated onto copper foil current collector, and dried at 60 °C for 8 h at vacuum condition. CR2025 coin-type cells were assembled with graphite electrode, lithium foil counter electrode, electrolyte and separator. The $LiCoO_2$/graphite batteries were assembled with $LiCoO_2$ cathode (80% $LiCoO_2$, 10% acetylene black, and 10% PVDF), graphite electrode, electrolyte and separator. All electrolyte preparation and cell assembly operations were carried out in an argon-filled glove box ($H_2O < 10$ ppm, $O_2 < 1$ ppm, Mikrouna). Before high temperature performance tests, the $LiCoO_2$/graphite batteries were stored at 85 °C for 4 h at vacuum condition.

2.2. Electrochemical measurements

Test cells were cycled with a Neware battery test system (BTS-51, Shenzhen, China) between 0.01 V and 2 V (vs. Li/Li^+) at a current mode of 0.1C. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (CHI604E, Chenhua, Shanghai, China) at a scan rate of $0.1 \, mV \, s^{-1}$. Electrochemical impedance spectroscopy (EIS) was measured immediately with frequency ranging from 0.1 Hz to 1 MHz at the initial and the last cycle.

2.3. SEI analysis

After charge-discharge cycling measurements, the batteries were disassembled in an argon-filled glove box to analyze the microstructure and chemical compositions of the SEI film. The morphologies of the graphite electrodes were observed by scanning electron microscopy (SEM, JSM5600LV, JEOL). The IR spectra were recorded by Fourier Transform Infrared Spectrophotometer (FTIR, Nicolet 6700, Thermol Fisher).

2.4. Theoretical calculations

All the calculations were performed using the Gaussian 09 program package [10]. The geometries of the organic carbonates, sulfite, and sulfates were optimized by B3LYP/6–311 + g(d, p) method. Besides, the frontier molecular orbital energy of each organic molecule was also calculated.

3. Results and discussion

3.1. Structures of sulfuric esters

DTD, 1,2-PS and 1,3-PCS are structurally similar to the commonly used organic carbonate EC. The carbonate of EC is replaced by sulfate in the structures of DTD and 1,3-PCS. Fig. 1 shows the optimized structures of the carbonates and sulfuric esters at the B3LYP/6–311 + g (d, p) level. The bond lengths, bond angles and LUMO energies of carbonates and sulfuric esters were calculated as listed in Table 1. The differences in bond lengths and angles are mainly derived from carbon and sulfur atom. The bond lengths of S-O were longer than those of C-O, and the angles of O_3-S_1-O_4 were smaller than those of O_3-C_1-O_4, resulting in easier breakage of S-O. Moreover, the LUMO energies of DTD, 1,2-PS and 1,3-PCS were much lower than those of organic solvents EC, DMC and EMC, which indicates that DTD, 1,2-PS and 1,3-PCS should be better electron acceptors and easier reduced on the graphite anode.
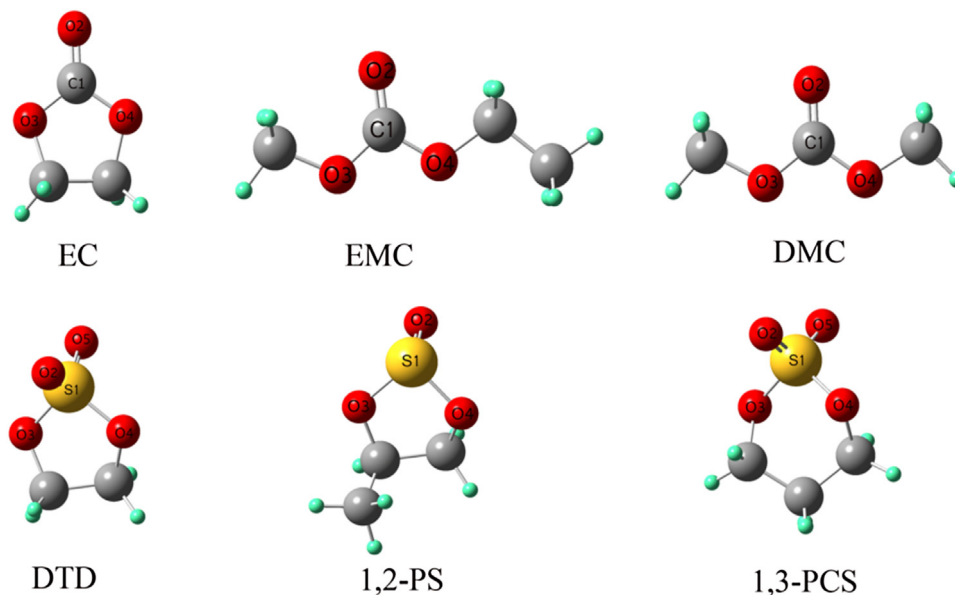

Fig. 1. Optimized structures of solvents and additives at the B3LYP/6–311 + g (d,p) level.