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Evaluation of di(2,2,2-trifluoroethyl) sulfite as a film-forming additive on the MCMB anode of lithium-ion batteries

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HIGHLIGHTS

- DTFES used as a new additive in the MCMB-based battery systems.
- DTFES participated in the formation of SEI on the surface of MCMB.
- DTFES enhanced the cycling performance of MCMB-based batteries.

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ABSTRACT

This study demonstrates a sulfur-based compound, di(2,2,2-trifluoroethyl) sulfite (DTFES), as a new solid electrolyte interphase (SEI) forming additive on mesocarbon microbeads (MCMB). When placed in the electrolyte, it can dramatically enhance the performance of lithium-ion batteries (LIBs). The capacity loss was significantly decreased from 17.4% to 6.3% after 100 charge-discharge cycles due to the addition of DTFES. Differential capacity (dQ/dV) versus voltage (V) analysis showed that DTFES was decomposed in advance versus to electrolyte solvents. The effects of DTFES were characterized by charge-discharge testing, electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). These results indicate that the SEI film formed on MCMB by DTFES plays an important role in LIBs performance. Their subsequent reaction pathways are proposed in the paper.

1. Introduction

Lithium ion batteries (LIBs) have been applied widely in many electronic devices including, cell phones, computers, cameras and electric vehicles, due to their excellent performance versus other battery types [1,2]. Electrolytes in cells play an important effect on the performance of LIBs. Commercial electrolyte solutions consist of conventional organic carbonate solvents, lithium hexafluorophosphate ($LiPF_6$) and some additives. In the initial charging stage, solvents such as ethylene carbonate (EC) are reduced at the anode surface and form a solid electrolyte interphase (SEI) film on the anode electrode [3]. It is well known that the presence of the SEI film prevents further decomposition of the electrolyte solvent and enables the subsequent charge-discharge process [3,4]. Electrolyte additives can significantly improve the SEI properties and improve the performance of the cells including, cycle life, safety, energy density, etc [5–9].

Numerous SEI forming additives have been developed in recent years, including unsaturated additives (like vinyl compounds, vinylene carbonate (VC)) [10,11], sulfur-based additives (like butylene sulfite (BS), 1,3,2-dioxathiolane-2,2-dioxide (DTD)) [12,13], boron-based additives [14], isocyanate-based additives [15] and ionic additives [16]. Of these, vinyl compounds and sulfur-based compounds have attracted significant attention. One of the most effective SEI-forming additives VC, it has been used widely in LIBs. Nevertheless, VC has a negative effect on cell performance due to its polymerization on the cathode [17].

Sulfur-based compounds are another promising SEI-forming additive on the anode electrode. Chen et al. [12] evaluated butylene sulfite (BS) as a film-forming additive in a propylene carbonate (PC)-based electrolyte. Their study demonstrated that a 5 vol% concentration of BS can effectively suppress the co-intercalation of PC into graphite. Sano et al. [13] employed the

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cyclic sulfate 1,3,2-dioxathiolane-2,2-dioxide (DTD) as an electrolyte additive in EC:PC (1:1, vol%). Samples containing 5 wt% DTD in the electrolyte had dramatically improved cycling performance LIBs, with a capacity retention >85% after 400 cycles. Xia et al. [18] reported cyclic sulfates including ethylene sulfate, trimethylene sulfate and propylene sulfate as electrolyte additive in LIBs. Their study showed that using DTD alone as an additive can compete with VC.

Here, a sulfur-based compound named, di(2,2,2-trifluoroethyl) sulfite (DTFES), was synthesized and used as a new SEI-forming additive for LIBs. This offers better cyclic performance than VC and DTD. The effect of DTFES was assessed by charge-discharge testing, electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM).

2. Experimental

2.1. Synthesis of di(2,2,2-trifluoroethyl) sulfite

A three-necked flask was fitted with a dropping funnel protected with a calcium chloride tube, a mechanical stirrer, and a condenser. This was connected to a trap for absorption of hydrogen chloride. The 119.0 g (1.0 mol) of thionyl chloride was placed in the flask and 222.0 g (2.2 mol) of 2,2,2-trifluoroethanol was placed in the dropping funnel. The flask was cooled in an ice bath, and 2,2,2-trifluoroethanol was added dropwise while stirring over 4 h. After all the 2,2,2-trifluoroethanol was added, the mixture was refluxed for 1 h to complete the reaction and remove the residual hydrogen chloride. The crude di(2,2,2-trifluoroethyl) sulfite was distilled to collect the fraction boiling at 135 °C. The yield of di(2,2,2-trifluoroethyl) sulfite is 196 g. The di(2,2,2-trifluoroethyl) sulfite was further purified as follows: the fraction was neutralized by addition of alkaline solution, and then the organic phase was sequentially separated and dried over anhydrous $MgSO_4$ and a molecular sieve The dried organic phase was fractionated using Ni-Cr as a packing column. The purity of the di(2,2,2-trifluoroethyl) sulfite is 99.9% (by GC), and the water content is 17.6 ppm by Karl-Fischer titration.

2.2. Electrolyte and electrode preparation

We obtained 1.0 M $LiPF_6$-EC/EMC/DMC (1:1:1, wt%, remarked as LIB124) and 1.0 M $LiPF_6$-PC/DMC (1:2, wt%, remarked as LIB009) electrolytes from Dongguan Shanshan Battery Materials Co., Ltd. (China). The VC and DTD additives were purchased from Fujian Chuangxin Science and Technology Development Co., Ltd. (China). The DTFES, DTD and VC were combined with the electrolytes in an argon-filled glove box with ≤1 ppm water and oxygen. The amount of DTD and VC added to the electrolyte was 2 wt% as in Ref. [18]. The commercial MCMB powder was obtained from Shenzhen BTR nano-science and technology Co., Ltd. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powder was obtained from Pulead Technology Industry Co., Ltd. The MCMB electrodes were composed of 80 wt% MCMB, 10 wt% carbon black and 10 wt% poly(vinylidene fluoride) (PVDF). These were prepared by mixing these materials in *N*-methylpyrrolidone (NMP), coating and pressing these mixtures onto a copper foil. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes were composed of 80 wt% $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, 10 wt% carbon black and 10 wt% poly(vinylidene fluoride) (PVDF). They were prepared by mixing these materials in *N*-methylpyrrolidone (NMP) solvent, coating and pressing these mixtures onto an aluminum foil. Both of these electrodes were then dried at 110 °C for 12 h. The resulting electrodes were used to fabricate CR2025 MCMB/Li and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/Li coin half-cells to evaluate the effect of DTFES on the electrochemical activity of the cell.

2.3. Measurements

A CT2001A tester (Landt Instruments, Wuhan, China) was employed to assess the charge-discharge activity of the batteries. After formation involving 0.1 C cycling 2 times followed by 0.2 C cycling 3 times as well as, aging for 10 h, the MCMB/Li cells were charged to 2.0 V at a constant-current of 0.2 C. Discharge then occurred to 0.005 V at 0.2 C. After formation involving 0.2 C cycling 3 times and aging for 10 h, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/Li cells were charged to 4.3 V at a constant-current of 0.2 C. Discharge then occurred to 3.0 V at 0.2 C. Electrochemical impedance spectra (EIS) was conducted at 100 kHz to 0.01 Hz with impedance amplitude of 10 mV using a frequency response analyzer (VSP, Bio-Logic SAS, France) after the first charge-discharge cycle and after 100 charge-discharge cycles with the MCMB/Li cells charged to 2.0 V.

After completing charge-discharge cycle testing, the cells were disassembled in a glove box in an Ar atmosphere both electrodes were rinsed at least 5 times with DMC to remove any residual electrolyte material. The electrodes were then dried for 12 h in vacuum at room temperature. To better understand the surface chemistries on the MCMB surfaces, the chemical compositions of the surface layers at the electrode/electrolyte interfaces for cells with and without the DTFES additive were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The FTIR spectra were obtained on a NICOLET Is5 (ThermoFisher Scientific) spectrometer within 400–4000 cm^{-1} using transmittance mode. The XPS spectra were obtained on ESCALAB 250Xi (Thermo Scientific) using Al Ka radiation. The peak energy of the carbon containment (i.e., C1s = 284.8 eV) was used to calibrate the binding energies. TEM characterized the surface morphology of the MCMB powder (Tecnai G20, FEI).

3. Results and discussion

The effects of the DTFES additive on the cycling performance of MCMB/Li cells were evaluated (Fig. 1). The best cycling performance is achieved when the concentration of DTFES is 0.5 wt%. The discharge capacity of the cells increases with the increasing DTFES concentration, and reaches a maximum at 0.5 wt%. This reduces again at 1.0 wt%. To analyze the specific effect of DTFES on the cells, we separated the data of 0.5 wt% DTFES versus cells without additive (Fig. 1(b)). The capacities of the cells at the initial discharge with and without DTFES were 352.6 mA h g^{-1} and 344.6 mA h g^{-1}, respectively. The cells with DTFES in the electrolyte had significantly improved cycling performance. After 100 charge-discharge cycles, the discharge capacity of the battery with DTFES was 330.4 mA h g^{-1}. The discharge capacity obtained for the cell without additives was only 284.8 mA h g^{-1}. As such, the capacity losses are 6.3% and 17.4% for cells with and without 0.5 wt% DTFES, respectively.

Fig. 2 shows the first discharge and charge curves and differential capacity (dQ/dV) versus voltage (V) for the MCMB/Li cells employing electrolytes with and without 0.5 wt% DTFES during formation. A small plateau at ~1.6 V can be observed during the first discharge for the cell with 0.5 wt% DTFES (Fig. 2(a)). The peak at ~1.6 V is also observed in the dQ/dV versus V curve (Fig. 2(b)). This may correspond to the reduction of DTFES on the MCMB surface. We used PC as the solvent to further confirm the reduction of DTFES on the MCMB surface. The potential vs. capacity plot of MCMB/Li cells using $LiPF_6$-PC/DMC (1:2, wt%) electrolytes in the first cycle with and without DTFES are presented in Fig. S1. For the base electrolyte, there is a long plateau at ~0.86 V (vs. Li/Li^+) for the discharging process, this corresponds to the PC decomposition and