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Enhanced high-voltage cyclability of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$-based pouch cells via lithium difluorophosphate introducing as electrolyte additive

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ABSTRACT

To meet the electrolyte requirements for high-voltage cathode materials, lithium difluorophosphate (LiDFP) is evaluated as a lithium salt additive for the conventional carbonate-based electrolyte system. The $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite pouch cells containing 1 wt% LiDFP delivers a discharge capacity retention of 93.8% over 100 cycles operated at a cut-off voltage of 4.5 V, which is higher than the 43.2% of that without additive; and its average discharge capacity can reach around 118.9 mAh g^{-1} at 5 C, while the reference cell only achieves 93.4 mAh g^{-1}. Herein, the electrochemical impedance spectroscopy results obtained from the two- and three-electrode pouch cells indicate that LiDFP can respectively suppress impedance growth of two electrodes during cycling. The spectroscopic analysis demonstrates that the cathode surface can be modified by the additive and a stable solid electrolyte interface (SEI) is also formed on the anode surface by the presence of LiDFP in the electrolyte. Additionally, the capacity retention for the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Si-C pouch cell is also noticeably enhanced from ~3.5% to 67.2% by adding 1 wt% LiDFP into the electrolyte over 200 cycles operated at 4.5 V.

1. Introduction

A wide range of negative and positive electrode materials have been thoroughly investigated and commonly used in commercial batteries [1–9]. Lithium nickel manganese cobalt oxide with the general composition, $LiNi_xMn_yCo_zO_2$ ($x + y + z = 1$), is a popular high-voltage material, where the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$, in particular, has entered the spotlight because of its high energy and good electrochemical performance at a high charge state [10–14]. However, NCM-based cells also suffer several fatal issues, especially the insufficient capacity retention under a high charge cutoff voltage (>4.5 V vs Li^+/Li). It is generally accepted that traditional electrolyte oxidative decomposition is one of the main causes of the severe capacity fading during cycling [15–17]. Therefore, the demand for a stable electrolyte has become a high priority for the practical application of these materials at high voltages. The design and synthesis of electrolyte solution with intrinsic stability to tolerate high voltage, and the exploitation of suitable electrolyte additives to enhance the stability the electrode-electrolyte interphase are the two common approaches to suppress electrolyte decomposition [12,18–21].

In light of the techno-economic perspective for the latter method, various compounds, such as triethlylphosphite and tris(2,2,2-trifluoroethyl) phosphate [10], 3,3′-sulfonyldipropionitrile [22], diphenyl disulfide [23], dopamine [24] and fumaronitrile [25] have been investigated as high-voltage electrolyte additives, confirming their positive impact on the electrochemical properties of lithium-ion batteries. Among the various high-voltage electrolyte additives, some newly developed lithium salts have also been tested as electrolyte additives and provided noteworthy benefits for the lithium-ion cells under high-voltage. Li et al. [26] discussed the

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effects of lithium bis(oxalate)borate (LiBOB) on 5 V high-voltage cells using $LiNi_{0.5}Mn_{1.5}O_4$ as the cathode, and the research shown that an excellent cycling stability, good rate capability performance and favorable electrochemical properties for the half cell can be achieved due to the electrolyte containing LiBOB having a high oxidation stability. Zuo et al. [27] reported that for an electrolyte with 1 wt% lithium tetrafluoroborate ($LiBF_4$), the capacity retention of a $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cell after 100 cycles was greatly improved from 29.2% to 90.1% in the voltage range of 3.0–4.5 V. The improved performances of the cell are attributed to the interface layer components on both electrodes modified by $LiBF_4$. Hu et al. [28] showed that lithium difluoro(oxalato)borate (LiDFOB) was good for formation a stable interphase film on a $LiCoPO_4$ electrode and improved its high-voltage cycle stability. As performed by Zhang et al. [29], for Li/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cells using the electrolyte containing 0.2 wt% LiBOB or 0.5 wt% LiDFOB cycled at 4.6 V, the cyclic stability can be greatly enhanced due to the additive modifying the surface films and suppressing the oxidation reactions of electrolyte on the positive electrode surface. Also, as presently reported by Zhou and his co-workers [30], the LiODFB/$LiBF_4$ blend salt electrolyte is a promising candidate because of its excellent affinity to the high-voltage $LiNi_{0.5}Mn_{1.5}O_4$-based cells in a wide electrochemical window. Other lithium salts additives, such as lithium difluoro(sulfato)borate [31], lithium bis(fluorosulfonyl) imide [32] and lithium bis(2-methyl-2-fluoromalonato)borate (LiBMFMB) [33] were also investigated. Meanwhile, a novel lithium salt named lithium difluorophosphate (LiDFP) has been reported to enhance the high rate capability performance of graphite electrodes, as it can attend the formation of a high ionically conductive and stable surface film on graphite [34]. Additionally, Yang et al. [35] demonstrated that the improvement of low temperature performance at 0 °C for $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells was attributed to the modification of LiDFP in the graphite anode. Although the aforementioned literatures have mentioned the positive role of LiDFP in improving some performances for cell with graphite electrode at normal charge cutoff voltage, limited literature data is available for its benefit to the high-voltage performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$-based full cells. In this work, the impacts of LiDFP on the electrochemical performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite full pouch cells cycled at different charge cut-off voltages were specifically analyzed by electrochemical measurements and spectroscopic techniques. Additionally, Si-C composite materials have been under intensive investigation as a hopeful anode for high energy density lithium-ion batteries [36,37]. In this study, $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Si-C pouch cells were also assembled and different electrolytes were used to evaluate the impact of LiDFP on the high-voltage electrochemical performance.

2. Experimental

2.1. Electrolyte and cell preparation

The reference electrolyte was composed of 1.0 M lithium hexafluorophosphate ($LiPF_6$) ethylene carbonate (EC)/diethyl carbonate (DEC) = 1/3 (weight-based ratio). For the electrolyte main components, lithium salt and carbonate solvents were supplied by Guangzhou Tinci Materials Technology Co., Ltd., China (both are battery grade). LiDFP used in this work was purchased from Nippon Shokubai Co., Ltd., Japan within a molecular purity >99%. The LiDFP-based electrolytes were prepared by adding different weight ratios of additive into the reference electrolyte and shaking until uniformity in a nitrogen-filled glove box. The water (less than 20 ppm) and hydrofluoric acid (less than 50 ppm) contents in those samples were determined by auto moisture titration instrument (Karl Fischer 831 Metrohm, Swiss) and automatic potentiometric titrator (Karl Fischer 798 Metrohm, Swiss), respectively. $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ powder was purchased from Ningbo Jinhe New Materials Co., Ltd., China. The $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ electrode had a formulation of 93 wt% active material, 3 wt% carbon black and 4 wt % polyvinylidene fluoride (PVDF). Graphite and Si-C (S420, the theoretical specific capacity is 420 mAh g^{-1}) powders were purchased from Jiangxi Zichen Technology Co., Ltd. and BTR Battery Materials Co., Ltd., China, respectively. The graphite and Si-C electrodes had a formulation of 95 wt% active material, 1.5 wt% carboxymethyl cellulose (CMC), 1 wt% Super-P and 2.5 wt% styrene butadiene rubber (SBR). In addition, the separator was purchased from Shenzhen Senior Technology Material Co., Ltd., China. The $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Si-C pouch cells were assembled with the graphite or Si-C as the negative electrode and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ as the positive electrode, respectively. The $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Li/graphite three-electrode pouch batteries were assembled with graphite as the negative electrode, Li metal foil as the reference electrode and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ as the positive electrode, respectively. In this work, the detailed parameters about the electrode materials loading level and electrolyte injection weight for each of these $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Si-C pouch cells have been listed in Table 1.

2.2. Electrochemical tests and characterization analysis

Electrochemical properties were carried out in two-electrode and three-electrode pouch batteries under room temperature. The initial activation process of pouch cell was operated at different current rates of 0.1, 0.2 and 0.5 C for three charge-discharge cycles, respectively. For the rate capability experiment, the cell charged at constant current of 1 C and then discharged under various current varying from 0.2 C to 5 C in the voltage ranges of 3.0–4.5 V. The constant current cycling experiment was conducted under a current of 1 C in the different charge cut-off voltage of 4.2 V and 4.5 V. The above electrochemical tests were performed by a battery test system (Neware, CT-3008). Additionally, a nearly fully charged state of 4.5 V was controlled for cell impedance analysis. The alternating current (AC) impedance measurement was performed by frequency response analyzer (Solartron 1455 A). The frequency range is 100 kHz to 0.02 Hz with a sinusoidal signal of 10 mV in amplitude. The directing current (DC) impedance measurement was carried out on battery internal resistance tester (JT-VRC8). The AC impedance of the three-electrode cells and DC impedance of the two-electrode cells were recorded at the 3rd, 50th and 100th cycles. The $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ and graphite electrodes were obtained from the two-electrode cells in different electrolytes cycled between 3.0 and 4.5 V after 100 cycles. Both electrodes were washed by dimethyl carbonate (DMC), then transferred into the glove box transition warehouse until dried. The morphologies of different electrodes surface were observed by Field emission scanning electron microscopy (SEM, Carl Zeiss Supra 40) and transmission electron microscopy (TEM, JEM-2100). The surface chemical compositions analysis was performed by energy dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250).

3. Results and discussion

3.1. Electrochemical properties of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite pouch full cells

$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite pouch full cells containing various ratios of LiDFP in the $LiPF_6$-EC/DEC-based electrolyte were cycled under a current rate of 1.0 C. Fig. 1a shows the cycling results of cells