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Tris(trimethylsilyl) borate as an electrolyte additive for high-voltage lithium-ion batteries using $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode

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The influence of tris(trimethylsilyl) borate (TMSB) as an electrolyte additive on lithium ion cells have been studied using $Li/LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells at a higher voltage, 4.7 V versus Li/Li^+. 1 wt% TMSB can dramatically reduce the capacity fading that occurs during cycling at room temperature (RT) and elevated temperature (60 °C). After 150 cycles at 1 C rate (1 C = 278 mAh/g), the capacity retention of $Li/LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is up to near 72% in the electrolyte with TMSB added, while it is only about 35% in the baseline electrolyte. The electrochemical behaviors, the surface chemistry and structure of $Li/LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode are characterized with charge/discharge test, linear sweep voltammetry (LSV), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS), thermal gravimetric analyses (TGA), scanning electron microscope (SEM) and transmission electron microscopy (TEM). These analysis results reveal that the addition of TMSB is able to protectively modify the electrode CEI film in a manner that suppresses electrolyte decomposition and degradation of electrode surface structure, even though at both a higher voltage of 4.7 V and an elevated temperature of 60 °C.

1. Introduction

Lithium ion batteries (LIBs) are used as a green energy source for portable electronic devices, electric vehicles (EVs), hybrid electric vehicles (HEVs) and plug in hybrid electric vehicle (PHEV) owing to their high energy density and long lifetimes [1]. And more stringent performances are requested for electric cars applications than for portable electronics applications. Batteries employed in EV, HEV and PHEV require higher energy densities, wider working temperature ranges and longer lifespan. Currently, the layered $Li[Ni–Co–Mn]O_2$ oxide cathode materials are being used to power batteries. Benefited from its high capacity, good structural stability and relatively low cost, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is one of the most promising cathode materials for Li-ion batteries used for electric cars [2,3]. Unfortunately, the transition metal ions of $LiNi_xCo_yMn_{1-x-y}O_2$ could catalyze electrolyte decomposition reaction due to its high oxidizing activity, which results in severe capacity fading of the battery [4–6]. Especially, when the battery is used at a relatively high temperature (>45 °C), dramatic losses of its energy and power happen, leading to a short serving life time [7–9]. And there will be more gas generated in the cells at higher temperature, bringing about security problems. Working at the state of either high voltage or high temperature, Li-ion batteries tend to suffer from serious capacity fading with the electrolyte and electrode destabilized. Therefore, improvement of battery high-temperature performance at high-voltage state is extremely important and urgently demanded.

Introducing cathode electrolyte interface (CEI) film additives play a guiding role in improving cyclic performance of cathode material in Li-ion batteries, and it is one of the most economical and effective methods [10–13]. These additives can be oxidized before solvents decomposition, and their oxidation products form a passivation layer on the electrode surface to prevent the further decomposition of electrolyte and electrode [14,15]. Tris (trimethylsilyl) borate (TMSB) has been investigated as a protective cathode additive for increasing the cycle performance of several high voltage cathodes materials including $LiMn_2O_4$ (4.5 V) [16], $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (4.4 V) [15], $LiNi_{0.5}Mn_{1.5}O_4$ (4.9 V) [17] and layered lithium-rich oxide cathode $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ (4.8 V) [18]. And TMSB can also be applied as an effective electrolyte additive to raise the cycle life of $LiMn_2O_4$ and $LiFePO_4$ cathode Li-ion batteries at 55 °C [16,19]. As to our knowledge, the use of TMSB additive for $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode in state of both high voltage and high temperature has not been reported yet.

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In this work, Tris(trimethylsilyl) borate (TMSB) is firstly taken on as an additive to enhance the cyclability of Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells at 4.7 V upon cycling at room temperature and elevated temperature (60 °C). Electrochemistry methods and ex-situ analysis are used to understand the improvement mechanism of Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells with TMSB.

2. Experimental

2.1. Preparation

The blank electrolyte used was 1.0 M $LiPF_6$ dissolved in ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1 wt% ratio, obtained from Dongguan Shanshan battery material Co., Ltd., China). To this electrolyte, 1 wt% Tris(trimethylsilyl) borate (TMSB, Fujian Chuangxin Science and Develops Co., Ltd., China, 99.95%) was added. The $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrodes with an active mass loading of about 2.75 mg/cm^2 were prepared by mixing the $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ powder (Ningbo Jinhe New materials Co., Ltd., China, 80 wt%), carbon black (10 wt%) and poly(vinylidene fluoride) (PVDF 10 wt%) in N-methylpyrrolidone (NMP) solvent. The mixed slurry was coated onto aluminum foil and dried under vacuum at 120 °C for 12 h. The dried electrode was then compressed by a roller to make a compact and smooth film structure at room temperature. The electrode disks were then punched out of the coated foil sheets and weighted. The electrode disks were then dried under vacuum at 100 °C overnight before being transferred to an Ar-filled glove box for cell assembly. Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells were fabricated with 2025-coin type cells in the argon-filled glove box using Celgard 2325 as the separator.

2.2. Electrochemical measurements

The charge–discharge performances were tested on Neware battery test system (CT3008). The cells were stored in a 25 or 60 °C temperature controlled box, and were charged and discharged at 0.2 C 3 cycles, 0.5 C 3 cycles, then cycled at 1 C (1 C=278 mAh/g) rate between 3.0 and 4.7 V.

Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were performed on CHI660D electrochemical workstation at 25.0 ± 1 °C. EIS measurements were conducted on $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$/Li half-cells with charging to 4.7 V after one cycle and 150 cycles at 1 C charging rate. AC impedance spectra were collected with 10 points per decade from 100 kHz to 10 mHz with a signal amplitude of 10 mV. LSV was carried out in a self-made three-electrode glass with Pt as the working electrode and Li foils as the counter and the reference electrodes between 3.0 and 5.8 V at a sweep rate of 0.1 mV/s.

2.3. Physical characterization

To analyze the composition and microstructure of the electrodes after charge–discharge cycling measurements, the cells were disassembled and the $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrodes were washed with dimethyl carbonate (DMC) solvent to remove residual electrolyte, dried in the argon-filled glove box. The chemical composition of the surface layer on the $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific) with Al Kα line as an X-ray source. The graphite peak at 284.8 eV was used as a reference for the final adjustment of the energy scale in the spectra. Thermal gravimetric analyses (TGA) were performed with heating rate of 10 °C/min on a NETZSCH STA 449C simultaneous TG-DSC instrument. Scanning electron microscope (SEM SU8010) equipped with an energy dispersive spectroscopy (EDS) detector was used to characterize the morphology of the electrodes. Transmission electron microscope (TEM JEM-2010, JEOL) was used to study the film on the $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ electrodes.

3. Results and discussion

3.1. Electrochemical performance

The effects of TMSB additive on the cycle performance of Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells charged to 4.7 V at 1 C rate are evaluated both at RT and 60 °C (Figs. 1 and 2). For the Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells without additive, the charge–discharge profiles (Figs. 1a and 2a) became more deformed and shortened with the growth of the electrochemical cycling. Consequently, the separation between the average charging and discharging voltages was enhanced markedly by the cycling. That means a polarization growth during the cycling. The opposite, the Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells with TMSB additive shows stable charge–discharge profiles on the succeeding cycles (Figs. 1b and 2b), where the coulombic efficiency (CE) of the cells both at RT and 60 °C is maintained more steady during cycles, as shown in Figs. 1(c) and 2(c). At RT, it can be found that both the cells display a high CE over 150 cycles. And the cell containing the TMSB additive exhibits a higher CE than that of the cell with the conventional electrolyte. At 60 °C, the CE of the cell containing 1 wt% TMSB additive is about 98.8% at the 150th cycle, while the CE of the cell with the conventional electrolyte is about 90.5% at the same cycle number. The higher CE and less fluctuation of CE during the cycling of the cell containing the TMSB additive indicate that the TMSB additive will affect the formation of the cathode electrolyte interface (CEI) film in a favorable way. The cycling performances of Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells without and with additive are shown as a relation of cycling number in Figs. 1(d) and 2(d). The capacity retentions of Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells with TMSB containing in the electrolyte retain about 71.8% after 150 cycles with a capacity fade from 168.2 mAh/g down to 120 mAh/g, compared to the cells without additive in the electrolyte that retain only 34.8% with a rapid capacity fades from 169.3 mAh/g down to 59.3 mAh/g. The cycling performance of Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells with and without TMSB at elevated temperature (60 °C) is characterized at 1 C rate as shown in Fig. 2(d). While the capacity varies from 163.1 to 118.0 mAh/g with capacity retention of the cell 71.7% at the 150th cycle, the cell without TMSB shows a significant capacity drop from 150.6 mAh/g to 53.5 mAh/g with capacity retention only 35.5% after 150 cycles. Results show that the discharge capacity of the Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells with electrolyte containing TMSB decreases less. That is to say, cycling performances are improved remarkably with TMSB additive both at RT and 60 °C at the high voltage state (4.7 V). To investigate the possible capacity contribution from insertion reaction of carbon black, the cycling performance of Li-ion cell with carbon black only electrode is shown in Fig. 3 at RT. Electrodes with only carbon black exhibit lower initial discharge capacity of about 4 mAh/g with constant current 50 μA, which indicates carbon black contributes little capacity to Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells at a voltage range of 3.0–4.7 V. It is consistent with the results reported in the literature [20].

Electrochemical impedance spectroscopy (EIS) technique was used to study the interfacial impedance changes of Li/$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cells at RT. Fig. 4(a) and (b) presents AC impedance changes of the 1st and 150th cycle of the cells with and without TMSB. Each curve contains two semicircles from high to medium frequency range and a straight line in the low frequency range (Warburg resistance). The first semicircle is ascribed to the surface film resistance of cell and the second semicircle is attributed to the charge-transfer resistance of cell [21,22]. In Fig. 4(a), while the impedance values of the first semicircles for cells with and without additive are almost the same, the impedance