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Improved high-voltage performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode with Tris(2,2,2-trifluoroethyl) phosphite as electrolyte additive

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ABSTRACT

Tris(2,2,2-trifluoroethyl) phosphite (TTFEP) is investigated as an electrolyte additive to improve the electrochemical performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode at high operating voltage (4.6 V). Charge/discharge measurements demonstrate that TTFEP is effective to improve the cycling stability and rate capability of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode. The capacity retention of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/Li cell with 1% TTFEP-containing electrolyte reaches up to 85.4% after 100 cycles at 0.5C (1C = 160 mA g^{-1}), while that of the cell with the baseline electrolyte (1 M $LiPF_6$ in EC/DMC electrolyte) only remains 74.2%. Moreover, the discharge capacity of the cathode with 1% TTFEP-containing electrolyte could maintain around 112.0 mAh g^{-1} at 4C. Based on the characterization of electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), a protective interphase film formed on the cathode surface can be found due to the preferential oxidation of TTFEP, which inhibits the electrolyte decomposition and mitigates the cathode structural destruction, leading to the improved electrochemical performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode at high voltage.

1. Introduction

Lithium-ion batteries (LIBs) have been extensively applied in portable electronic devices in virtue of their long cyclic life, high energy density and environmental benignity, whereas their energy density cannot satisfy the increasing demands for the large-scale applications of electric vehicles/hybrid electric vehicles (EVs/HEVs) and other energy storage systems [1–5]. To improve the energy density of LIBs, one of the most effective ways is to search for novel cathode materials with high operating voltage [6–10]. Currently, the layered oxide material, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, is considered as one of the most promising cathodes due to its appropriate operating voltage, low cost, high reversible capacity and safety [11–14]. Unfortunately, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode usually exhibits unsatisfied electrochemical performance under high voltage with serious self-discharge at charging state, which is mainly caused by the oxidation decomposition of carbonate-based electrolyte and serious crystal destruction of cathode during long cycling under high voltage [15–17].

To resolve the problems mentioned above, several approaches, such as surface modification, novel solvents substitution and functional additives introduction in electrolytes, have been proposed to enhance the high-voltage electrochemical performance of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode materials. Specifically, the surface modification chiefly includes ion-doping and surface-coating with metal oxides, metal fluorides, Li^+-conductors, conductive second phases, graphene and so on [18–26], which are effective to improve the electrochemical performance but at the expense of specific capacity and cost. Novel solvent substitutions for the carbonate-based electrolyte mainly involve ionic liquids, sulfones, nitriles, and fluorinated carbonates considering their high oxidation potential, while their application was hindered severely for the poor compatibility, high viscosity and low ionic conductivity. [27–31]. Comparatively, applying electrolyte additives, such as phosphite, borate, phosphate, sulfate,

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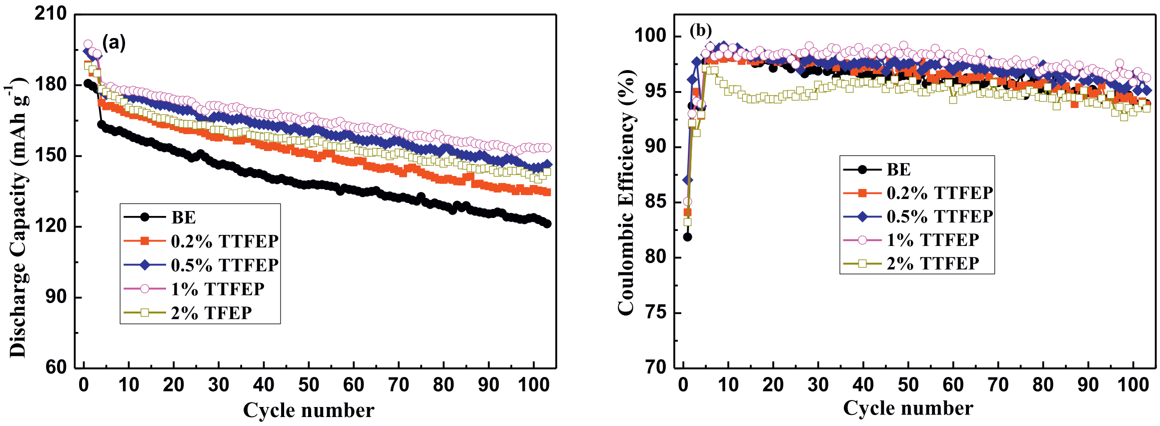

Fig. 1. Cyclic capability (a) and coulombic efficiency (b) of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/Li cells in BE electrolytes containing different contents of TTFEP.

nitrile-based compounds, to generate a protective film on the cathode surface is regarded as one of the most cost-efficient and effective methods to improve the high-voltage electrochemical performance of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode [32–38]. Recently, Pires et al. [39] reported the positive effect of Tris(2,2,2-trifluoroethyl) phosphite (TTFEP) as additive on the long cycling performance of layered Li-rich cathode since TTFEP could act as a catalyst to several surface reactions. He et al. [40] discovered that improved capacity retention and coulombic efficiency of Ni-rich layered cathode material ($LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$) was achieved in the TTFEP-containing electrolyte with the protective coating formed on the cathode surface. It is noteworthy that TTFEP was an effective electrolyte additive for high-voltage Li-ion battery cells as reported in these literatures. However, the effects of TTFEP additive on the electrochemical behavior of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode at high voltage have not been reported in detail.

In this work, TTFEP was investigated as an electrolyte additive for improving the electrochemical performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode at high operating voltage. The effect mechanism of TTFEP on the interface and electrochemical performance of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode was studied by electrochemical and ex-situ physical characterizations, including charge/discharge tests, chronoamperometry, storage tests, electrochemical impedance spectroscopy (EIS), scanning electron microscope (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The results indicated that incorporation of 1% TTFEP into the electrolyte could significantly improve the cycling stability and rate capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with a protective interphase film formed on the electrode surface.

2. Experimental section

2.1. Preparation of electrolytes and cell

The battery-grade ethylene carbonate (EC), dimethyl carbonate (DMC) solvents and lithium hexafluorophosphate ($LiPF_6$) were obtained from Guangzhou Tinci Materials Technology Co., Ltd, China, and the solvents were dehydrated by using 4A molecular sieves. Tris(2,2,2-trifluoroethyl) phosphite (TTFEP, 98%) was purchased from Suzhou Yacoo Science Co., Ltd (China) and used without further purification. The baseline electrolyte (BE) with 1.0 mol L^{-1} $LiPF_6$ dissolved in EC/DMC (1/2, in volume) mixed solution, and the TTFEP-containing electrolytes with various contents of 0.2, 0.5, 1, and 2% in the BE electrolyte were prepared in an argon-filled glove box (MBraun, Germany) with the content of H_2O and O_2 less than 5 ppm.

The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode materials were purchased from Hunan Shanshan Advanced Materials Co., Ltd (china). The cathode electrode was prepared by mixing $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (85 wt.%), acetylene black (5 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%) binder in N-methyl-pyrrolidone (NMP) solvent, which was coated on Al foil and dried at 120 °C for 12 h under vacuum. The dried electrode was punched into a round disk with diameter of 14 mm and compressed by a roller, and the average mass loading of active materials was about 3.5 mg cm^{-2}. The graphite electrode was prepared by coating a mixture slurry of graphite (90 wt.%), acetylene black (3 wt.%) and PVDF (7 wt.%) on copper foil. Then the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/Li or graphite/Li cells were assembled with CR2025-type coin cells in the argon-filled

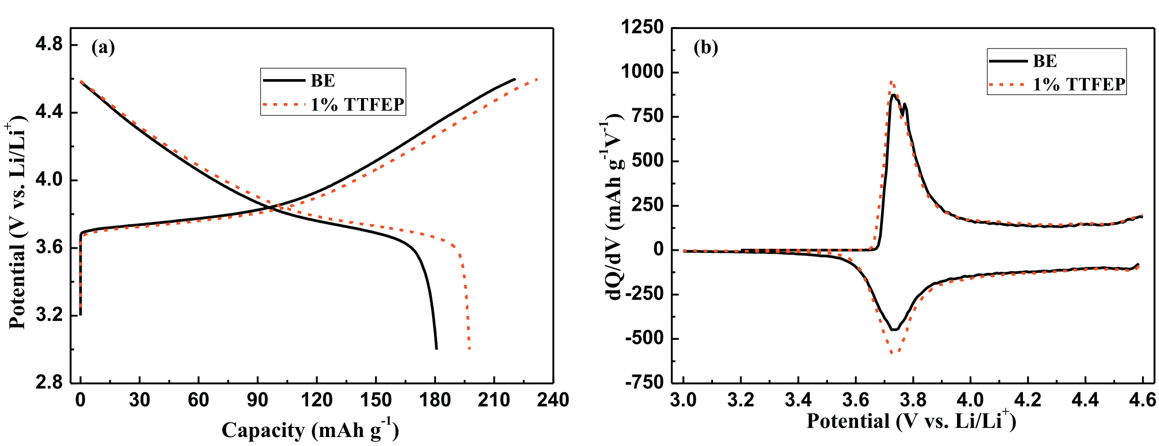

Fig. 2. The initial charge/discharge curves (a) and corresponding dQ/dV profiles (b) of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/Li cells cycled in the BE and 1% TTFEP-containing electrolyte.