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Tris(trimethylsilyl) borate as an electrolyte additive to improve the cyclability of $LiMn_2O_4$ cathode for lithium-ion battery

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HIGHLIGHTS

- TMSB used as additive to improve cyclability of $LiMn_2O_4$ cathode lithium-ion battery.
- The lithium-ion battery containing TMSB shows excellent capacity retention at 55 °C.
- TMSB participated in the formation of SEI on the surface of electrode.
- Enhancement of cyclability of Li anode by TMSB additive.

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ABSTRACT

In order to overcome severe capacity fading of $LiMn_2O_4$ cathode lithium-ion battery, tris(trimethylsilyl) borate (TMSB) is used as an electrolyte additive. With 0.5 wt% TMSB addition into the electrolyte (EC/DMC with 1 M $LiPF_6$), the capacity retention is significantly improved at both room temperature and 55 °C. The effects of the TMSB on the $LiMn_2O_4$ electrode are investigated via a combination of cyclability, capacity retention of high temperature storage, electrochemical impedance spectroscopy (EIS), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Based on these results, it is suggested that the improved cyclability of the cells containing the TMSB additive is mainly originated from the participation in the formation of solid electrolyte interface (SEI) on the surface of electrode, the dissolution of LiF out of the SEI and the enhancement of cyclability of Li anode.

1. Introduction

During the past few decades, lithium-ion batteries (LIBs) have been developed as the power source for electric vehicles (EVs) and plug-in hybrid electric vehicles (HEVs) [1,2], which generally require a long cycle life and high capacity retention. As the performance, price, and safety of lithium-ion batteries mainly depend on the properties of the cathode materials, much attention has been paid to the search for high capacity, cheap and safe cathode materials [1,2]. Among all candidate cathode materials, $LiMn_2O_4$ becomes the promising cathode material for commercial usage due to the low cost, safety, cyclability and benign to environment. However, the batteries used spinel $LiMn_2O_4$ as cathode material have problems with severe capacity fading and poor cycling, especially at elevated temperature [3–6]. The main reason for capacity fading is the dissolution of Mn^{2+} from spinel $LiMn_2O_4$ into electrolyte due to the presence of HF, which is formed by the decomposition of lithium hexafluorophosphate ($LiPF_6$) salt with residual water in the electrolyte [7–10]. In order to suppress Mn^{2+} dissolution, material scientists are doing many endeavor to develop new stable $LiMn_2O_4$ materials by using different methods: (1) partial Mn substitution with different transition metals, (2) partial anion substitution O with F, and (3) metal oxide surface coatings [11]. However, the improvement of the electrode materials involves complex synthetic process and high cost.

The use of electrolyte additives would be one of the most effective and economic methods to suppress the capacity fading and improve the cycling performance of $LiMn_2O_4$ lithium-ion batteries. Usually, the amount of an electrolyte additive is no more than 5 wt% while its presence significantly improves the cyclability of LIBs. Sun et al. [12] reported tris(pentafluorophenyl) borane (TPFPB) as an anion receptor electrolyte additive for

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$LiMn_2O_4$/Li battery. The $LiMn_2O_4$/Li battery with the $LiPF_6$-based electrolyte containing 0.1 M TPFPB additive exhibited more superior capacity retention and coulomb efficiency at 55 °C than the battery without additive. Park et al. [13] used fluoroethylene carbonate (FEC) as an electrolyte additive to improve the capacity retention of $LiMn_2O_4$/graphite LIBs. With 2 wt% FEC addition into the electrolyte (EC/DEC/PC with 1 M $LiPF_6$), the capacity retention at 60 °C after 130 cycles was significantly improved by about 20%. The heptamethyldisilazane used as an additive to improve the stability of the electrolyte (EC/EMC/PC with 1 M $LiPF_6$) and cycling performance of $LiMn_2O_4$ batteries was also reported [14].

In this paper, tris(trimethylsilyl) borate (TMSB), was used as electrolyte additive to improve the performance of $LiMn_2O_4$/Li battery with 1 M $LiPF_6$ in EC/DMC (1:1, w:w). The effects of TMSB on the improvement of electrolyte thermal stability and cycle life of the $LiMn_2O_4$/Li battery were investigated.

2. Experimental

Battery-grade ethylene carbonate (EC), dimethyl carbonate (DMC) and $LiPF_6$ were purchased from Shenzhen Capchem Chemicals Co., Ltd., China, and used without further purification. Battery-grade tris(trimethylsilyl) borate was purchased from Fujian Chuangxin Science and Technology Develops Co., Ltd., China, and used without further purification. The electrolytes of 1 M $LiPF_6$ in a 1:1 (weight ratio) EC/DMC with and without 0.5 wt% TMSB additive were prepared in an argon-filled glove box, in which the oxygen and water content were less than 1 ppm.

$LiMn_2O_4$ cathode materials were purchased from Hunan Reshine New Material Co., Ltd., China. The $LiMn_2O_4$ electrodes were prepared by mixing the $LiMn_2O_4$ powder (90 wt%), carbon black (5 wt%) and poly(vinylidene fluoride) (PVDF 5 wt%) in N-methylpyrrolidone (NMP) solvent. The mixed slurry was coated onto aluminum foil and dried at 80 °C for 0.5 h, then dried at 125 °C at 1.5 h. The dried electrode was then compressed by a roller to make a compact and smooth film structure at room temperature. The electrode disks (1.5386 cm^2) were then punched out of the coated foil sheets and weighted. $LiMn_2O_4$/Li half cells were fabricated with 2016-coin type cells in the argon-filled glove box using Celgard 2400 as the separator.

The charge–discharge behavior of the cells was tested on Land CT2001A tester (Wuhan, China) at the constant current mode over the range of 3.0–4.5 V. The constant current mode of 1.0 C was carried out at both room temperature and 55 °C. At the initial and last cycled galvanostatic measurement, electrochemical impedance spectroscopy (EIS) of the cell was observed immediately under full charged condition. EIS measurement was accomplished by coupling the potentiostat with an Autolab frequency response analyzer locked in an amplifier and an impedance phase analyzer. A sinusoidal amplitude modulation was used over the frequency range from 0.1 Hz to 1 MHz.

The storage test of the $LiMn_2O_4$/Li cells at 80 °C was carried out followed by the procedure: the assembled cells were charged with a constant current of 0.5 C–4.5 V, and then the full charged cells were put into an oven at 80 °C for 24 h, 48 h and 72 h, respectively. After that, the full charged cells were discharged to 3.0 V at room temperature. The tested cells were all under the full-charged status.

The lithium cycling performance was carried out by using sealed 2016-coin type Li/stainless steel cells at 55 °C in our experiments. The electrolytes of 1 M $LiPF_6$ in a 1:1 (weight ratio) EC/DMC with and without 0.5 wt% TMSB additive were used. The electrodes were separated by Celgard 2400 film. An excess of lithium (3.6 C cm^{-2}) was first galvanostatically plated on the surface of the stainless steel electrode, and then consumed by galvanostatic cycling of a fraction of the original excess lithium (0.36 C cm^{-2}). The experiment was stopped as a sharp change in dissolution potential (0.3 V *vs.* Li/Li^+) happened.

To analyze the element composition and microstructure of the $LiMn_2O_4$ electrodes after charge–discharge cycling measurements, the cells were disassembled in an argon-filled glove box. The $LiMn_2O_4$ electrodes were washed with anhydrous DMC several times to remove residual salts, and then dried in vacuum oven for 2 h at room temperature. Scanning electron microscope (SEM, Ultra 55, Carl Zeiss) was used to observe the morphology of the $LiMn_2O_4$ electrodes. X-ray diffraction (XRD) patterns were recorded at room temperature using a X-ray diffractometer (XRD, D/max-2200/PC, Japan) by continuous scanning in the 2θ range of 5–80°. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Kratos Axis UltraDLD spectrometer (Kratos Analytical-A Shimadzu group company) using a monochromatic Al Kα radiation ($h\gamma$ = 1486.6 eV). The analyzer used hybrid magnification mode (both electrostatic and magnetic) and the take-off angle was 90°. The pass energy was fixed at 40.0 eV to ensure high resolution and sensitivity. Binding energy was calibrated by using the containment carbon (C1s = 2 84.8 eV). Peak assignment was made based on detailed curve fitting of the recorded spectra using Gaussian-Gauss2 peak shapes and a Shirley function background correction. The Kratos charge neutralizer system was used on all specimens except the conductive samples.

3. Results and discussion

The $LiMn_2O_4$/Li half cells were assembled containing 1 M $LiPF_6$ in EC/DMC (1:1, w:w) composite electrolytes without and with the presence of 0.5 wt% TMSB additive. The cells were cycled at 1.0 C rate under constant current conditions. The experiments were carried out at both room temperature and 55 °C. Fig. 1 shows the cycle performance of the $LiMn_2O_4$/Li cells at room temperature with different electrolytes. The cell with conventional electrolyte displayed about 23% capacity loss at the 180th cycle, while the cell containing 0.5 wt% TMSB additive showed only 5% capacity loss at the same cycle number. Fig. 2 shows coulombic efficiency (CE) of these cells. It can be found that both the cells exhibited a very high CE over 180 cycles. And the cell containing the TMSB additive exhibited a higher CE than that of the cell with the conventional electrolyte. The higher CE and less fluctuation of CE during the

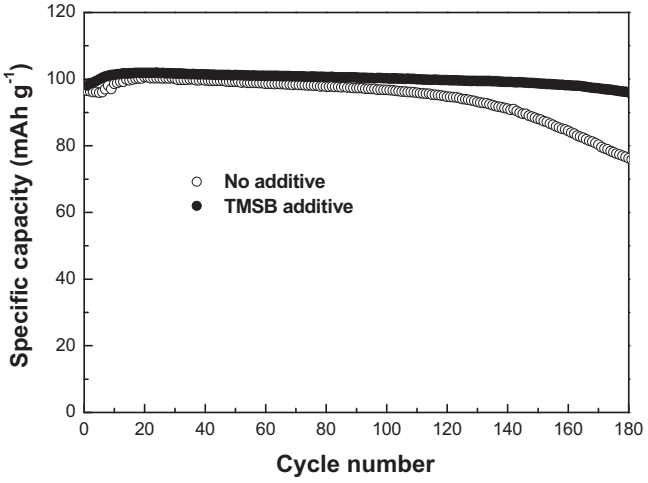

Fig. 1. Cycle performance of $LiMn_2O_4$/Li half cells using 1 M $LiPF_6$ in EC/DMC (1:1, w:w) as electrolytes with and without 0.5 wt% TMSB additive at room temperature. Charge–discharge rate was 1.0 C in the potential range of 3.0–4.5 V.