Electrochimica Acta 221 (2016) 107–114

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Lithium difluorophosphate as an additive to improve the low temperature performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells

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ARTICLE INFO

Article history:
Received 30 July 2016
Received in revised form 2 October 2016
Accepted 6 October 2016
Available online 7 October 2016

Keywords:
Lithium difluorophosphate
electrolyte additive
low temperature
$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells

ABSTRACT

Lithium difluorophosphate ($LiPO_2F_2$) was used as an electrolyte additive to promote the low temperature performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells. The impact of $LiPO_2F_2$ on the solid electrolyte interface (SEI) film-formation on electrodes was demonstrated by various electrochemical methods and microscopy techniques, such as transmission electron microscopy (TEM), scanning electron microscope (SEM) as well as X-ray photoelectron spectroscopy (XPS), in the pouch cells and half cells. The results showed that the cells containing 1% $LiPO_2F_2$ performed 71.9% (−20 °C) and 57.93% (−30 °C) of initial capacity, while the cells without $LiPO_2F_2$ discharged only 49.41% and 9.6% of initial capacity under the same condition. In addition, the enhancement of cyclic performance at 0 °C was attributed to a conductive and stable SEI film formed on the graphite by the sacrifice of $LiPO_2F_2$, which led to a low impedance and richer content of LiF and Li_2CO_3 in SEI components, as depicted in XPS.

1. Introduction

Owing to the characteristics of high energy density, memory-less effects and being environment friendly, lithium ion batteries (LIBs) have been widely used as an essential device for digital communication, electric vehicles and so on [1–3]. Unfortunately, LIBs are often subjected to great capacity loss at low temperature, which restricts their application in cold climates [1]. Although the substantial failure mechanism is still in dispute, the main reasons which lead to the poor low temperature performance have been attributed to the following points; (i) increased viscosity and poor Li^+ conductivity, (ii) limitation of the SEI film-formation on graphite and the sluggish lithium kinetics over the SEI, (iii) the reduced diffusion of lithium ion in graphite, (iv) high polarization giving a rise to charge-transfer resistance on electrolyte-electrode interface [4,5]. In previous researches [6,7], many attempts were made to overcome the above barriers via optimizing solvent system or film-formation additives. Due to their high ionic conductivity and low viscosity, esters like ethyl propionate (EP), thyl acetate (EA) and methyl acetate (MA), are used as the co-solvent to enhance the cells performance at low temperature. However, the presence of linear carboxylic ester would affect long life cycle performance at an elevated temperature. From a comprehensive perspective, it is not a great option to use ester as the co-solvent. Due to its low melting point (−48.8 °C), propylene carbonate (PC) could expand the liquid temperature range of electrolyte [8]. But it is well known that PC, when used as a major solvent, will combine with lithium-ion co-inserting into graphite, which causes severe graphite exfoliation [9]. Whereas an appropriate concentration of PC in the electrolyte will have the slight negative influence on graphite, and more importantly, prevent ethylene carbonate (EC) from crystallizing out at low temperature. Changing electrolyte system is a feasible method to solve the problem of high viscosity and poor conductivity while it could not improve the sluggish diffusivity of lithium ion within the graphite. Adopting film-formation additive is beneficial to the intercalation of Li^+ into graphite. A majority of low temperature additives are fluorinated compound, since the reduction of fluorochemicals is prior to that of EC and modifies the surface morphology and SEI composition. Fluoroethylene carbonate (FEC) is most commonly used additive for low temperature [6,8]. In addition, some lithium salts like lithium tetrafluoroborate ($LiBF_4$) [10] and lithium bis(oxalato)borate (LiBOB) [11] also could promote the low temperature performance when used as the main salt or additive.

In this paper, we reported the lithium difluorophosphate ($LiPO_2F_2$) was used as an electrolyte additive to improve the low

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http://dx.doi.org/10.1016/j.electacta.2016.10.037

temperature performance of LIBs. According to the work by Ko-Eun Kim et al. [12], the high rate performance was strongly enhanced by the combination of $LiPO_2F_2$ and vinylene carbonate (VC). This work also revealed that $LiPO_2F_2$ could modify the SEI film formation on graphite, which led to a high ionic conductivity and stable SEI layer. Owing to the characteristics of $LiPO_2F_2$, we expect that $LiPO_2F_2$ can improve the low temperature performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells. Therefore, various electrochemical methods and spectroscopic techniques were employed to demonstrate the effect of $LiPO_2F_2$ on low temperature performance and illustrate the reaction mechanism of $LiPO_2F_2$ at both electrodes.

2. Experiment

2.1. Sample preparation

The following chemicals are all purchased from Guangzhou Tinci Materials Technology Co., Ltd., China. A low-temperature type of electrolyte which was made by dissolving a 1 M $LiPF_6$ in ethylene carbonate (EC), ethylmethyl carbonate (EMC) and propylene carbonate (PC) with a 4:7:1 weight ratio was regarded as a reference electrolyte. Adding 1 wt.% $LiPO_2F_2$ (LG Co. Ltd, Korean) to the reference electrolyte was supposed to be the researched one.

A cathode slury was fabricated by mixing 94.5 wt.%$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (Shenzhen Tianjiao Tech. Co,. Ltd.), 1.5 wt.% polyvinylidene fluoride (PVDF) and 4.0 wt.% conductive carbon (Super-P). The anode electrode contained graphite (Shenzhen BTR Co,. Ltd.), Carboxymethyl Cellulose (CMC), Super-P and Polymerized Styrene Butadiene Rubber (SBR) with a 95.3:1.4:1.5:1.8 weight ratio. Both electrodes were dried at 120 °C for 10 hours under vacuum conditions before the cells assembled. The $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells were used to understand the impact of LiPO2F2 on low temperature performance. Moreover, in order to know the effect of $LiPO_2F_2$ on cathode and anode electrode, CR-2016 button cells made of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Li and graphite/Li, respectively, were used.

2.2. Electrochemical Measurements

Cyclic voltammograms (CV) curves were conducted on graphite/Li button cells with the scan rate of 0.05 $mV\,s^{-1}$ over a range of 0.01–3 V. The cells were measured by an electrochemical work station (CHI660, Chenhua, China). The charge-discharge cyclic performance at 0 °C and −20 °C was determined with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells through a battery test instrument (CT-3008W, Neware, China). A temperature controlling box (GDW-100L, SUOYATE, China) was used to maintain the environment temperature at diverse low temperature. Before the normal battery tests, the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells were charged to 3.85 V with a constant current (0.1 C) and then cycled 3 times with different rates of 0.1 C, 0.2 C and 0.5 C. After that, a low-temperature cycling test was followed by 100 cycles at 0.5 C rate from 2.75 V to 4.20 V. For the sake of the low temperature discharge ability, cells were cycled 3 times with a rate of 1 C at room-temperature before putting them in temperature controlling box with different temperatures of 0 °C,−10 °C,−20 °C and −30 °C for 4 hours. And then the cells were discharged at 0.5 C rate to 2.75 V. Indeed, DC resistance (DCR) was also examined at the above temperatures. Before DCR measurement, pouch cells were charged to 100% SOC and then put them into the temperature controlling box at different temperatures for 4 hours and the last second voltage was recorded as U_1. The cells were discharged at a specific rate of 0.5 C for 10 seconds using the final second potential as U_2. Afterward, the DCR value was calculated by using the formula: $DCR = (U_2 - U_1)/I$. Electrochemical impedance spectroscopy (EIS) measurements were conducted with frequency response analyzer (FRA, Solartron 1455A, Solartron, England), CHI660 for $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells and half cells. For full cells, the EIS of 100th cycles at 0 °C was measured with 100% SOC (approximately 4.2 V) over a frequency range of 100 kHz to 20 mHz at an amplitude of 10 mV. For half cells, in order to form a stable SEI film and investigate the impact of $LiPO_2F_2$ on electrodes interface resistance, 3 cycles at a rate of 0.05 C at room temperature need to be taken prior to EIS measurement at 0 °C. The EIS test of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Li and graphite/Li half cells were performed at 4.2 V and 0.01 V, respectively.

2.3. Physical Characterization

To further figure out the characteristic of electrode surface, the cycled cells were disassembled in an argon-filed glovebox and the collected electrodes were rinsed with pure DMC for 3 times to remove the residual lithium salt and the electrolyte on electrodes surface. Then the samples were dried in glovebox for 12 hours and taken into an argon-filed bottle before the analysis. The surface morphology of the electrodes was observed by scanning electron microscopy (SEM, ZEISS Sigma500, Carl Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100HR, JEOL, Japan). The surface element composition of the electrodes were analyzed by X-ray photoelectron spectroscopy (XPS, AZIS SUPRA, Kratos, British) using the Al Kα line as the X-ray source.

3. Results

3.1. Electrochemical behavior of the electrolytes on graphite anode

In order to understand the impact of $LiPO_2F_2$ on graphite, Li/graphite half cell was used to investigate the electrochemical behavior of the electrolyte which contains 1% $LiPO_2F_2$. As shown in

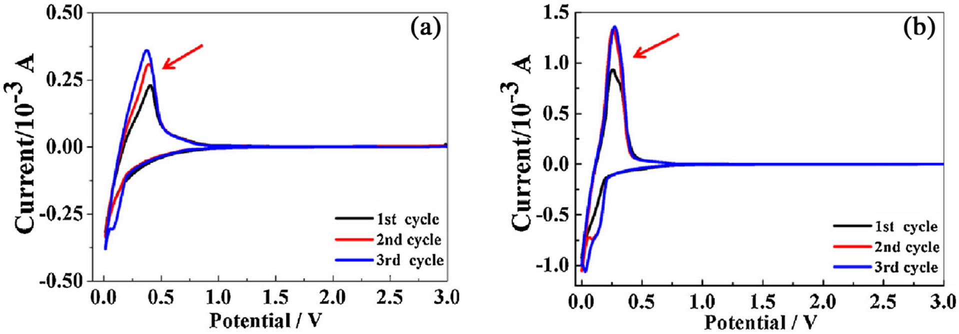

Fig. 1. Cyclic voltammograms of graphite/Li half cells in 1 M $LiPF_6$ dissolved in EC: EMC: PC (4:7:1, wt %) with different contents of $LiPO_2F_2$: (a) without $LiPO_2F_2$; (b) with 1% $LiPO_2F_2$ with a scan rate of 0.05 $mV\,s^{-1}$.