Journal of Power Sources 380 (2018) 149–157

Contents lists available at ScienceDirect

Journal of Power Sources

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

Toward a stable solid-electrolyte-interfaces on nickel-rich cathodes: $LiPO_2F_2$ salt-type additive and its working mechanism for $LiNi_{0.5}Mn_{0.25}Co_{0.25}O_2$ cathodes

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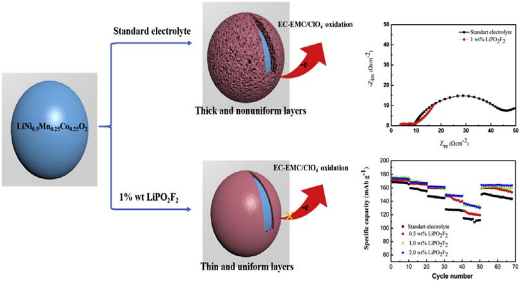
HIGHLIGHTS

- Lithium difluorophosphate ($LiPO_2F_2$) is a salt-type additive for LNMC.
- Cathode film generated by $LiPO_2F_2$ is thin, robust and low interfacial resistance.
- $LiPO_2F_2$ improves the cyclic and rate stability of LNMC.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Lithium difluorophosphate ($LiPO_2F_2$)
Electrolyte additives
Cathodes
Li-ion batteries

ABSTRACT

Although the $LiNi_{0.5}Mn_{0.25}Co_{0.25}O_2$ holds the merits of high theoretical capacities and a relatively high operating voltage, the battery performance suffers from the severe cycling decay due to the unstable solid electrolyte interface on the cathode. Herein, we present $LiPO_2F_2$ as a salt-type electrolyte additive to enhance the cycling stability of large-size crystallite $LiNi_{0.5}Mn_{0.25}Co_{0.25}O_2$ cathodes. Results demonstrate that 1 wt% $LiPO_2F_2$ can significantly improve not only the initial coulombic efficiency by 3%, but also the cycling stability and rate capability at 25 °C. Furthermore, the discharge capacity of $LiNi_{0.5}Mn_{0.25}Co_{0.25}O_2$ cathodes still maintain 156 mAh g^{-1} after 100 cycles even when the temperature increases to 55 °C. In-depth experimental characterization and theoretical calculation indicate that a new stable and thin (e.g. 15–20 nm) film formed on the surface of the cathodes, with composition of $LiPO_2F_2$, LiF, etc., which significantly reduces charge transfer impedance of the electrodes, and therefore significantly improves the cycling and rate performance of $LiNi_{0.5}Mn_{0.25}Co_{0.25}O_2$.

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https://doi.org/10.1016/j.jpowsour.2018.01.041
Received 16 November 2017; Received in revised form 27 December 2017; Accepted 17 January 2018

1. Introduction

Lithium-ion batteries (LIBs) become important in our daily life due to their wide application in portable electronic devices such as mobiles, laptops, etc. and electric vehicles. There are many challenges in developing battery chemistry in order to satisfy the demands in, for example, hybrid electric vehicles, plug-in electric vehicles, electric aircraft, etc. [1].

The battery energy is determined by the battery voltage and capacity, which is further determined by electrode potential and specific capacities of electrode materials. As we all know, the capacity of cathode materials is generally considered to be the bottle-neck in determining the battery capacity since the capacity of anode materials can be easily obtained higher than 300 mAh g^{-1} (e.g. C_6) while most of cathode materials is lower than 200 mAh g^{-1}. Therefore, in order to increase both electrode potential and the specific capacity, a new class of cathode materials such as $LiMO_2$ (M = Mn, Ni, Co), nickel-rich layered lithium transition-metal oxides ($LiNi_{1-x}M_xO_2$ with M = transition metal) have been exploited and investigated [2–4]. However, these materials are suffered from poor cycling stability due to their reaction with electrolyte at higher state of charge (SOC), especially at elevated temperature [5,6]. Among, the commercial ternary $LiMO_2$-based (M = Ni, Co and Mn) materials are considered to be the mostly promising cathode materials. However, these materials also exhibit continuous capacity loss due to secondary particles fatigue and intergranular crack formation which reduce the surface contact area between neighboring primary particles further resulting in the increase of the impedance for electronic and ionic transport [7,8]. Furthermore, residual H_2O induced from battery manufacturing process [9] will react with $LiPF_6$ to form LiF and Li_xPOF_y. This reaction can be described as (1–2) shown below [10,11].

$$LiPF_6 + H_2O = LiF + POF_3 + HF \tag{1}$$

$$POF_3 + Li^+ + ne^- = LiF + Li_xPOF_y \tag{2}$$

Various methods have been proposed to depress the side reactions at the interface between electrode and electrolyte, e.g., optimization of the particle size and surface modification such as coating [12–15]. It was found that when the crystallite $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) materials were synthesized with a grain size of 2–3 μm, the side-reactions between the cathode materials and the electrolyte could be significantly reduced, and the cycling stability of the batteries was highly improved compared with those conventional polycrystalline materials [16]. In the meanwhile, the thickness of the coating layer should be optimized. When the thickness of the coating layer is too high, e.g., the weight ratio of the coating layer is higher than 3 wt%, the decrease of the energy density and rate capability of the electrode materials becomes obviously. Apart from material modification, electrolyte additives development is another efficient strategy to improve the battery performance. There are some attractive examples in literature which describe some novel salt-type film-forming additives such as lithium difluoro(oxalate)borate (LiODFB) [17], lithium tetrafluorooxalatophosphate (LiFOP) [18,19], lithium 4-pyridyl trimethyl borate (LPTB) and lithium catechol dimethyl borate ((LiCDMB) [20,21], which can be sacrificially oxidized at the cathode surface prior to solvents oxidation decomposition. The subsequent products deposit on the cathode surface and form a compact thin layer which dramatically suppress the further oxidation of the electrolyte components.

Kim et al. demonstrated that combining $LiPO_2F_2$ with the organic additive vinylene carbonate (VC) can effectively modify the properties of the electrode/electrolyte interface to increase electron/ion transport rate, thereby significantly improving the charge/discharge performance of NMC/graphite cells [22]. Similar work has been reported by Yang *et al* [23]. Moreover, these deposited layers can protect the cathode electrode from metal dissolution.

Although some progress has been made with respect to $LiPO_2F_2$ additives, as far as we know, no studies have been reported on working mechanism of $LiPO_2F_2$ in nickel-based Li-ion batteries. In the present work, we investigate the influence of $LiPO_2F_2$ salt on the performance of $LiNi_{0.5}Mn_{0.25}Co_{0.25}O_2$-based cells with the electrolyte of 1 M $LiClO_4$ with EC and EMC solvent. Results show that the capacity retention is highly improved to be 95.3% after 200 cycles. The surface chemistries and morphologies of the cathode electrode cycled in the electrolyte with 1 wt% $LiPO_2F_2$ have been characterized via XPS, SEM and TEM techniques. The working mechanism of $LiPO_2F_2$ additives is proposed on the basis of theoretical calculations.

2. Experimental section

2.1. Electrolyte preparation

$LiClO_4$ salt (Morita Chemical Industries (Zhangjiagang) Co. Ltd., China) was used as the electrolyte salt instead of $LiPF_6$ in order to avoid the influence of salt decompositions. Ethylene carbonate (EC)/Ethyl methyl carbonate (EMC) (3:7 in wt.% ratio) was purchased from Zhuhai Smooth Way New Materials Co. Ltd. $LiPO_2F_2$ was purchased from Zhejiang Sinochem Lantian Co. Ltd (China). Electrolytes were prepared in the glovebox under Ar atmosphere ($H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm). A set of electrolytes with various amount of the $LiPO_2F_2$ salt (0 wt%, 0.5 wt%, 1.0 wt%, and 2.0 wt%) were prepared on the basis of EC/EMC and $LiClO_4$ (1 M). The conductivity of the electrolytes was tested by the conductivity meter (INESA, DDS-307, China).

2.2. Electrochemical measurements

All the electrochemical experiments were performed on CR2025 coin cells. Working electrodes were prepared by stirring a mixture of the active material $LiNi_{0.5}Co_{0.25}Mn_{0.25}O_2$ (provided by Xiamen Tungsten Co. Ltd., China), polyvinylidene floride (PVdF) and acetylene black with a ratio of 80:10:10 wt% in N-methyl-2-pyrrolidone. The homogeneous slurry was coated onto Al disk (diameter = 14 mm) and dried at 120 °C in vacuum condition. The averaged loading of active material was 3.5 mg cm^{-2}. The counter electrode was a standard lithium disk with a diameter of 15.8 mm. The ratio of electrolyte is approximately 100 μL in each battery. The electrochemical performance of the cells were measured with galvanostatic charge/discharge cycles under various current densities in the voltage range of 3.0–4.3 V on a Lanhe CT2001A battery tester at 25 °C. All cells were performed three formation cycles with C/10 rate for both charge and discharge. Cells show a good consistency and deliver almost the same initial discharge capacity of ~175 mAh g^{-1}. The electrochemical impedance spectra (EIS) were used to measure the impedance of the cells after charging to 3.9 V followed with 2 h relaxation to reach a quasi-equilibrium state (Open circuit voltage (OCV) = 3.9 V). The EIS measurements were conducted on a Versa STAT MV Multichannel potentiostat/galvanostat equipment with a potentiostatic mode using an AC signal of 5 mV from 100 kHz to 10 mHz.

2.3. Material characterization

Scanning electron microscopy (SEM) images were measured on S-4800 (Hitachi, Japan) microscopy, operating at 15 kV. Transmission electron microscopy (TEM) were conducted on a Tecnai F30 (Philip-FEI, Netherlands) apparatus, operating at 300 kV. Samples were placed in acetone and ultrasonically treated for 10 min to obtain a homogeneous dispersion. Two drops of the solution were then placed on standard copper mesh. X-ray photoelectron spectroscopy (XPS) measurements were equipped with a Quantum 2000 ESCA spectrometer (Physical Electronics, USA) with monochromatic Al Kα radiation (hυ = 1486.6 eV), operating at 23.2 W and in a vacuum of $< 10^{-8}$ Torr. The cells were dismantled in a glove box under Argon atmosphere. The dismantled electrodes were then transferred into the XPS vacuum