



An investigation of functionalized electrolyte using succinonitrile additive for high voltage lithium-ion batteries



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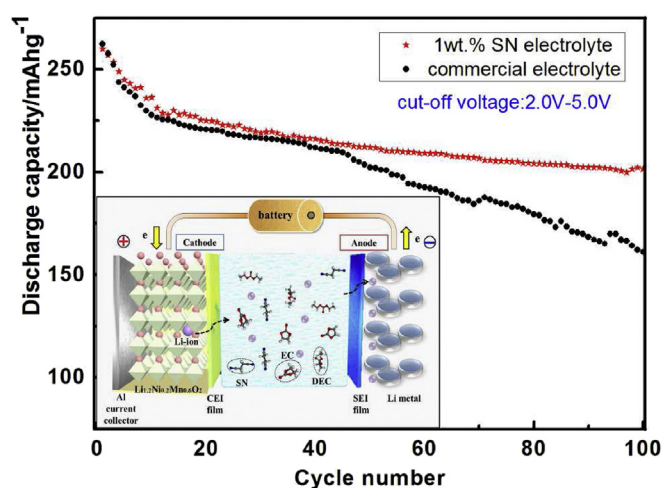
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HIGHLIGHTS

- The SN-based electrolytes show better thermal stability and wider electrochemical window.
- The effects of SN on the electrochemical performances of LIBs have been investigated.
- The 1 wt % SN-containing electrolyte improves cycle performance of LNMO batteries.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 July 2015

Received in revised form

27 October 2015

Accepted 28 October 2015

Available online 13 December 2015

ABSTRACT

Succinonitrile (SN) has been used as functional additive to improve the thermal stability and broaden the oxidation electrochemical window of commercial electrolyte 1 M LiPF₆/EC/DEC (1:1, by volume) for high-voltage LIBs (cathode: Li_{1.2}Ni_{0.2}Mn_{0.6}O₂, anode: Li). 1 wt % SN-based electrolyte showed a wide electrochemical oxidation window of 5.4 V vs Li⁺/Li and excellent thermal stability demonstrated by thermogravimetry (TG) and X-ray photoelectron spectroscopy (XPS), as well as theoretical analysis according to molecular orbital theory. The LNMO (Li_{1.2}Ni_{0.2}Mn_{0.6}O₂) battery with 1 wt % SN-based electrolyte showed better cyclability and capacity retention when charged to higher cut-off voltage. The improved battery performance is mainly attributed to the formation of uniform cathode electrolyte interface (CEI)

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Keywords:

Succinonitrile
High voltage
Thermal stability
Cathode electrolyte interface

formed by interfacial reactions between the LNMO cathode and electrolyte. The outcome of this work and the continuous research on this subject can generate critical knowledge for designing thermal stability electrolytes for large format lithium-ion batteries.

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1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronic devices since their commercialization. To satisfy the forceful motive power requirement of electric vehicle (EVs), hybrid electric vehicles (HEVs) and smart grid, developing high-voltage LIBs is a key approach to promote the energy density [1]. Currently, high-voltage cathode materials such as LiCoPO_4 and LiNiPO_4 can approach to 5 V or even higher [2,3]. However, the increased upper voltage limit may adversely affect cycle performance of entire battery system owing to the conventional EC-based electrolyte decomposing over time when the charge voltage reaches up to 4.5 V (vs. Li/Li^+) [4]. Although oxidization potentials vs. Li/Li^+ of organic carbonate solvents are usually reported about 5 V, the transition-metal ions of electrode could accelerate the electrolytes decomposition as catalyst, causing irreversible capacity fading [5].

There are mainly two ways to improve high-voltage electrolyte, finding new stable solvents and searching for novel functional additives. Fluorinated solvents, nitrile compounds, sulfone compounds, and ionic liquids are normally studied as new solvent or co-solvent. Our research group has reported several studies about high-voltage electrolyte based on tetramethylene sulfone [6–8]. As for additives, LiBOB is usually used for high-voltage cathode additives [9]. And other organic additives include sulfonate esters, phosphides, electrochemically polymerized monomers, carboxyl anhydrides and some special ethers [1]. Xiaolin Liao demonstrated that the 1% trimethylsilyl (TMSB)-containing electrolyte is helpful to suppress the self-discharge of the charged $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode results from the preferential oxidation of TMSB and the subsequent formation of a protective solid electrolyte interphase film [10]. H. Bouayad investigated glutaric anhydride (GA) as an electrolyte additive to improve the performances of $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells, benefited from a passivation film at the surface of both electrodes formed by GA degradation [11].

Among various high-voltage cathode materials, $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ is one of the most promising candidates which can provide much higher capacity than the traditional cathode materials such as LiCoO_2 and LiMn_2O_4 spinel [12–14]. However, the commercialized application of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ is hindered by challenges of voltage instability and capacity fading [15]. Furthermore, Ni and Mn also exhibit concentration partitions within the thin layer of surface reconstruction layer (SRL) in the cycled samples where Ni is almost depleted at the very surface of the SRL, indicating the preferential dissolution of Ni ions in the electrolyte [16].

LiPF_6 can be easily hydrolyzed when electrolyte exist water and acidic impurities [17]. As shown in Fig. 1, Nitriles can react with water in the acidic condition (H^+) as shown in the first two steps of

the equation, then water content drops down which relieves the process of LiPF_6 decomposed into HF at the same time. In total, not only does it can eliminate H_2O and HF which would promote Mn/Ni dissolution from the cathode, but also reduce the side reaction due to the formation of non-electrochemical active amide (RCONH_2).

Above all, previous researches have proved that nitrile-based electrolytes are very suitable for high-voltage cathodes. Yaser proposed that glutaronitrile is suitable for high energy/power Li-ion batteries as a co-solvent in thermally and electrochemically stable electrolyte mixtures at 14th International Meeting on Lithium Batteries [18]. Ue demonstrated that adiponitrile (ADN) exhibit could resist electrochemical oxidation at voltage of 5 V vs saturated calomel electrode (~ 8.3 vs Li^+/Li) [19]. Masatoshi Nagaham found that the EC/DMC/sebaconitrile (25:25:50 v/v) electrolyte containing 1 M LiBF_4 exhibited high electrochemical stability at 6.0 V on a LiFePO_4 electrode [20]. There have been some investigations about succinonitrile (SN) already, mainly focused on the polymer electrolyte [21–23], but only a few papers about SN for liquid electrolyte additive have been published [24–26]. Y. S. Kim proved that SN additives could improve the thermal stability of LiCoO_2 cells and used as overdischarge protection additives. Gu-Yeon Kim and co-workers investigated the effects of succinonitrile on the impedance of $\text{LiCoO}_2/\text{Graphite}$ pouch cells.

In this paper we studied succinonitrile (SN) as a commercial electrolyte additive to improve the cycling performance and thermal stability of the $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2/\text{Li}$ system in high cut-off voltage. Furthermore, the charge–discharge capacities of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2/\text{Li}$ with different cut-off voltages has been studied, and the effect of SN on the performance of the cells and reactions for the LNMO cathode were also discussed.

2. Experimental

2.1. Preparation of electrolyte systems

The electrolyte of 1 M LiPF_6 dissolved in ethylene carbonate (EC): Diethyl carbonate (DEC) (1:1, by volume), which was purchased from Zhangjiagang Guotai Huarong Chemical New Material Co. Ltd (named commercial electrolyte). SN-based electrolytes were prepared simply by mixing succinonitrile (SN, 99%, J&K Chemical) with the prepared electrolyte in various weight ratios in an argon-filled glovebox ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm, Mikrouna) and stirring for 24 h at room temperature. We have tested the water content of commercial electrolyte and 1wt % SN-based electrolyte by Karl-fisher method, 8.7 ppm and 7.6 ppm was measured respectively.

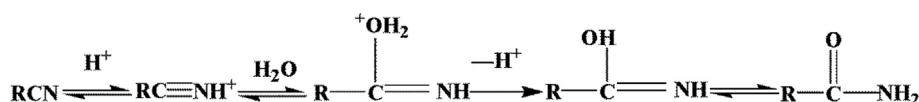


Fig. 1. The reaction mechanism of eliminating H_2O and HF by nitriles.

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