



1,3,6-Hexanetricarbonitrile as electrolyte additive for enhancing electrochemical performance of high voltage Li-rich layered oxide cathode



Long Wang^{a, b}, Yulin Ma^{a, b, *}, Qin Li^{a, b}, Zhenxin Zhou^{a, b}, Xinqun Cheng^{a, b}, Pengjian Zuo^{a, b}, Chunyu Du^{a, b}, Yunzhi Gao^{a, b, **}, Geping Yin^{a, b}

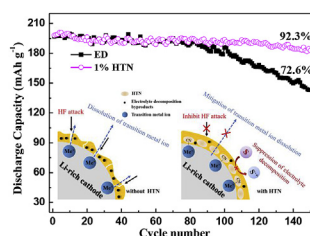
^a MIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, Harbin Institute of Technology, Harbin 150001, China

^b Institute of Advanced Chemical Power Sources, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

HIGHLIGHTS

- HTN improve the electrochemical performances of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ cathode.
- The effects of HTN on cathode surface properties were investigated at high voltage.
- A stable film formed on cathode surface with interaction between $\text{C}\equiv\text{N}$ and metal ion.

GRAPHICAL ABSTRACT



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ABSTRACT

1,3,6-Hexanetricarbonitrile (HTN) has been investigated as an electrolyte additive to improve the electrochemical performance of the $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ cathode at high operating voltage (4.8 V). Linear sweep voltammetry (LSV) results indicate that HTN can improve the oxidation potential of the electrolyte. The influences of HTN on the electrochemical behaviors and surface properties of the cathode at high voltage have been investigated by galvanostatic charge/discharge test, electrochemical impedance spectroscopy (EIS), and ex-situ physical characterizations. Charge–discharge results demonstrate that the capacity retention of the $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ cathode in 1% HTN-containing electrolyte after 150 cycles at 0.5 C is improved to 92.3%, which is much higher than that in the standard electrolyte (ED). Combined with the theoretical calculation, ICP tests, XRD and XPS analysis, more stable and homogeneous interface film is confirmed to form on the cathode surface with incorporation of HTN, meanwhile, the electrolyte decomposition and the cathode structural destruction are restrained effectively upon cycling at high voltage, leading to improved electrochemical performance of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ cathode.

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1. Introduction

The requirements for high-energy lithium-ion batteries (LIBs) are growing rapidly with the development of hybrid electric vehicles (HEVs), electric vehicles (EVs), and other energy storage systems [1–3]. However, the commercial LIBs are far insufficient to

* Corresponding author. School of Chemistry and Chemical Engineering, Harbin Institute of Technology, No. 92, West Dazhi Street, Harbin 150001, China.

** Corresponding author.

E-mail addresses: mayulin@hit.edu.cn (Y. Ma), gao_yunzhihit@hit.edu.cn (Y. Gao).

meet these requirements. In order to promote the energy and power density of LIBs, many efforts have been focused on exploration of new cathode materials with high operating potential above 4.5 V (vs. Li/Li⁺) such as LiMn_{1-y-z}Ni_yCo_zO₂, LiMPO₄ (M = Mn, Co, Ni), layered Li-rich metal oxides (xLi₂MnO₃·(1-x)LiMO₂, M = Ni, Co, Mn), and LiNi_{0.5}Mn_{1.5}O₄ [4–11]. Among these materials, layered Li-rich metal oxides have received extensive attention because of their high reversible specific capacity (over 250 mAh g⁻¹), high operating potential, and low cost [12–14]. However, these layered Li-rich cathodes usually exhibit poor cycling and rate performance, which are mainly caused by structure destruction of the oxide cathodes and severe oxidative decomposition of carbonated-based electrolyte under high operating potential during cycling [15,16].

There are mainly two effective approaches to overcome the issues mentioned above, including stabilizing the structure of the cathode materials and improving the oxidative stability of electrolytes. The former is achieved mainly by surface modification, ions doping and composite designing [17–30]. Commonly, materials used for surface modification of Li-rich cathodes contain metal oxides [17–19], phosphates [20,21], and fluorides [14,22–24], while ions doping or substitution mainly involves alien ions doping in lithium site in lithium ion layers [25,26], metal ion site and oxygen site in transition metal layers [27–29]. Improving the oxidative stability of electrolytes could be realized by searching for new electrolyte systems to replace the conventional carbonate-based electrolytes or introducing functional additives into traditional electrolytes. The alternative solvents or co-solvents for carbonate-based electrolytes, such as fluorinated solvents, ionic liquids, nitriles, and sulfone compounds, have been widely investigated because of their wide voltage window and good safety [31–35]. However, the surface coating and ions doping are complex and costly, and the new developed solvents usually suffer inferior electrode compatibility and low ionic conductivity compared with the carbonate-based solvents, which greatly hinder the improvement of electrochemical performance for layered Li-rich metal oxides.

Introducing additives into the electrolytes to form protective interface films on the cathode surface is thought to be one of the effective and economical ways to enhance the electrochemical performance of layered Li-rich cathode materials, including tris(2,2,2-trifluoroethyl) phosphite (TTFP) [36], phenyl vinyl sulfone (PVS) [37], di-(2,2,2-trifluoroethyl)carbonate (DFDEC) [38], tris(trimethylsilyl) borate (TMSB) [39,40], tri(hexafluoro-iso-propyl) phosphate (HFIP) [41], tris(trimethylsilyl) phosphite (TMSP) [42], (trimethylsilyl)methanesulfonate (TMSOMs) [43], lithium bis(oxalato)borate (LiBOB) [44,45], lithium difluoro(oxalate)borate (LiDFOB) [46,47] and ethylene glycol bis(propionitrile) ether (EGBE) [48]. Among the numerous additives, nitrile-based compounds are particularly attractive for high-voltage cathodes due to their good thermal property, high oxidative stability, and low flammability [49–53]. Ji et al. [50] found that suberonitrile (SUN) as additive in the electrolyte improve significantly the cyclic performance of the Li[Li_{0.2}Ni_{0.56}Mn_{0.16}Co_{0.08}]O₂ cathode with 77.4% capacity retention compared with 66.8% for the reference system after 200 cycles at current density of 180 mA g⁻¹, which can be attributed to the cathode surface modification by the SUN adsorption. Song's group demonstrated that nitrile-based molecular improve the thermal stability of LiCoO₂/graphite cells without sacrificing performances by protecting the surface of the cathode material. Additionally, they also found that the nitrile ending groups can provide environments favorable to the Li⁺ penetration [51]. Cui et al. elaborated on the interfacial interaction between adiponitrile (AND) additive and the surface of LiNi_{0.5}Mn_{1.5}O₄ by the analyses of X-ray photoelectron spectroscopy and theoretical calculation, the results show that AND can contribute to the

formation of a protective and conductive interfacial film on the cathode surface, which suppress the further electrolyte decomposition and improve the cyclability and rate capability of the cathode [52]. Based on the strong interaction between the electropositivity of the cathode metal ion and the electronegativity of nitrile functional groups, the tri-nitriles based compound, 1,3,6-Hexanetricarbonitrile (HTN), is expected to provide more strong interaction between surface metal atoms and nitrile (-CN) groups and play positive effects on the interfacial reactions.

In this work, HTN was investigated as an electrolyte additive to improve the electrochemical performance of the Li_{1.2}Ni_{0.13}-Co_{0.13}Mn_{0.54}O₂ at high operating voltage for the first time. The cyclic stability and rate capacity of the cathode has been distinctly improved with 1% HTN-containing electrolyte. The influence mechanism of HTN was revealed further via electrochemical and physical characterizations, including differential capacity (dQ/dV) analysis, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental section

2.1. Preparation of electrolytes and cells

The electrolyte in this work consisting of 1 mol L⁻¹ LiPF₆ dissolving in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with 1:2 vol ratio was used as the standard electrolyte (ED). The solvents and lithium salt were battery-grade purchased from Guangzhou Tinci Materials Technology Co. Ltd., China. The 1,3,6-Hexanetricarbonitrile (HTN, 99%) solution was purchased from Suzhou Yacoo Science Co. Ltd (China) and used without further purification, which was added into ED in weight amounts of 1% to obtain HTN-containing electrolyte. All electrolytes were prepared in the glove box filled with Ar atmosphere and the contents of water and oxygen were controlled to be less than 5 ppm. All solvents were further purified by 4A type molecular sieve in this manuscript. The Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ cathode material was prepared through a high temperature solid phase reaction between Ni_{0.167}Co_{0.167}Mn_{0.666}CO₃ precursor and LiOH·H₂O, and the precursor was synthesized by a coprecipitation method. The detailed preparation process was provided in the [Supporting Information](#).

The cathode electrode was prepared by coating the mixture slurry of Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂, super P, and poly(vinylidene) fluoride (PVDF) with a weight ratio of 85:7.5:7.5 dispersed in anhydrous *N*-methyl-2-pyrrolidinone (NMP) onto aluminum current collector. The electrode sheet was heated at 120 °C for 12 h in a vacuum oven and then punched into round disks with a diameter of 1.4 cm. The mass loading of active material was between 3.5 and 4 mg cm⁻². The anode electrode was prepared by coating a mixture slurry of graphite, super P and PVDF with a weight ratio of 90:3:7 on copper foil. The Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂/Li or graphite/Li half-cells using lithium metal sheet with a diameter of 1.56 cm as the counter electrode and Celgard 2400 (with a diameter of 1.65 cm) as the separators were assembled in the argon-filled glove box.

2.2. Electrochemical characterization

Oxidation stability of the electrolytes with and without HTN were evaluated by linear sweep voltammetry (LSV) measurements, which were conducted using a three-electrode system with Pt working electrode and lithium metal as both counter and reference electrodes from open circle voltages (OCV) to 6.0 V (vs. Li/Li⁺) at a scanning rate of 1.0 mV s⁻¹. Cyclic voltammetry (CV) were conducted at a scanning rate of 0.1 mV s⁻¹ between 2.0 and 4.8 V using

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