



# Improving cyclic stability of lithium nickel manganese oxide cathode at elevated temperature by using dimethyl phenylphosphonite as electrolyte additive



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## HIGHLIGHTS

- DMPP is developed as an electrolyte additive for high voltage  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode.
- DMPP improves significantly cyclic stability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  at elevated temperature.
- Protective film on  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is formed due to the preferential oxidation of DMPP.
- Electrolyte decomposition and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  destruction is suppressed effectively by DMPP.

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## ABSTRACT

A novel electrolyte additive, dimethyl phenylphosphonite (DMPP), is reported in this paper to be able to improve significantly the cyclic stability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode of high voltage lithium ion battery at elevated temperature. When experiencing charge/discharge cycling at 50 °C with 1C ( $1\text{C} = 146.7 \text{ mAh g}^{-1}$ ) rate in a standard (STD) electrolyte (1.0 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC), EC/DMC = 1/2 in volume),  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  suffers serious discharge capacity decaying, with a capacity retention of 42% after 100 cycles. With adding 0.5% DMPP into the STD electrolyte, the capacity retention is increased to 91%. This improvement can be ascribed to the preferential oxidation of DMPP to the STD electrolyte and the subsequent formation of a protective film on  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , which suppresses the electrolyte decomposition and protects  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  from destruction. Theoretical calculations together with voltammetric analyses demonstrate the preferential oxidation of DMPP and the consequent suppression of electrolyte decomposition, while the observations from scanning electron microscopy, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy confirm the protection that DMPP provides for  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

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## 1. Introduction

Lithium ion battery has been widely used as power sources in the field of information technology [1–3], but its energy density needs to be further enhanced for the applications in large scale, such as in the field of electric vehicles. To enhance the energy density of lithium ion battery, much attention has been paid to developing high-voltage cathode materials.  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (4.9 V vs.  $\text{Li}/\text{Li}^+$ ) is one of the most promising high-voltage cathode

materials due to its low cost and non-toxicity [4–7]. However, the cyclic stability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is poor, especially at elevated temperature, which results from the electrolyte decomposition and the accompanying  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  destruction [2,3,8].

Several methods have been proposed to inhibit the detrimental reactions on the high-voltage cathode materials, including surface modification of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  with inorganic oxides such as  $\text{ZnO}$ ,  $\text{SiO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$  and  $\text{ZrP}_2\text{O}_7$  [9–12] and substitution for carbonates with more stable solvents [13–15]. The surface modification increases the cyclic stability but reduces the specific discharge capacity. Solvents like lactone and sulfone are more stable at 5 V (vs.  $\text{Li}/\text{Li}^+$ ) than carbonates, but most of them have high viscosity. Similarly to the protection that electrolyte additives provide for

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graphite anode through forming a solid electrolyte interphase (SEI), electrolyte additives have been demonstrated to be able to provide protection for  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode and thus improve the cyclic stability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  [2,3,16]. Apparently, the strategy of using electrolyte additive is easier to operate and yields less negative effects than other approaches to improve cyclic stability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

Many factors might affect the protection that electrolyte additives provide for  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . Among these factors, the molecular structure of the electrolyte additives is most important, which determines the oxidizable ability of the additives and the stability of the formed SEI [16]. To avoid the interference of electrolyte decomposition products, one of which is carbon dioxide, the additives should be oxidized before electrolyte decomposition. On the other hand, the oxidation decomposition products should be robust for forming a stable SEI and are expected to provide SEI with ionic conductivity. Therefore, it is necessary to select electrolyte additives with suitable molecular structure to form an effective SEI.

Phosphorus derivatives have been reported as electrolyte additives for high-voltage cathodes, including trimethyl phosphite (TMP) [17] and triphenyl phosphine (TPP) [18]. TMP was found to be able to improve the cyclic stability and the rate capability of  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$  up to 4.8 V (vs.  $\text{Li}/\text{Li}^+$ ), which was attributed to the SEI formed by TMP [17]. The improved rate capability might be related to the oxygen atoms in TMP, which contributes to lithium ion conductivity. However, the oxidation potential of TMP is higher than that of carbonate solvents [17]. TPP was found to be able to improve the cyclic stability of  $\text{LiMn}_2\text{O}_4$  to 4.8 V (vs.  $\text{Li}/\text{Li}^+$ ), which was attributed to the insulating film formed by TPP [18]. Compared to TMP, TPP is preferably oxidized (at around 3.68 V, vs.  $\text{Li}/\text{Li}^+$ ) and the phenyls in TPP is more robust than alkyls in TMP, and thus facilitates forming more protective film. However, the use of TPP increases the cell resistance due to the insulation of the protective film. In this study, we combined the advantages of TPP and TMP and proposed a novel electrolyte additive, dimethyl phenylphosphonite (DMPP), for improving cyclic stability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . The electrochemical tests and physical characterizations demonstrated that DMPP is an effective additive for the protection of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

## 2. Experimental

Battery-grade carbonate solvents and lithium hexafluorophosphate ( $\text{LiPF}_6$ ) were provided by Guangzhou Tinci Materials Technology Co., Ltd. Dimethyl phenylphosphonite (DMPP) was purchased from Alfa Aesar Technology Co. A standard electrolyte (STD, 1.0 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC), EC/DMC = 1/2, in volume) and DMPP as additive were used. The  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode was prepared by coating a slurry of 80 wt%  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (Sichuan Xinneng Advanced Material Co., China), 5 wt% acetylene carbon black, 5 wt% Super-P and 10 wt% PVDF binder on Al foil and dried in vacuum oven. Graphite electrode was prepared for evaluating the effect of DMPP, which was composed of 94.5% natural graphite, 1.0% super-p, 1.5% carboxymethyl cellulose, and 2.0% styrene butadiene rubber.

$\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  coin cells were fabricated in an Ar-filled glove box with prepared electrolytes,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode, lithium foil anode and Celgard 2025 separator. In the evaluation of cyclic stability, the cells were charged and discharged with 0.2C ( $1\text{C} = 146.7 \text{ mA g}^{-1}$ ) at room temperature for two cycles and then with 1C at room temperature or 50 °C for subsequent cycles on LAND test system (CT2001A, China).  $\text{Li}/\text{graphite}$  coin cells were also fabricated and charge/discharge tests were performed with 0.1C ( $1\text{C} = 372 \text{ mA h g}^{-1}$ ) at room temperature to evaluate the effect of DMPP on the graphite anode.

The linear sweep voltammetry (LSV), cyclic voltammetry (CV) were performed on Solartron-1480 instrument (England). LSV was carried out in an electrolytic cell using platinum disk (100  $\mu\text{m}$  in diameter) as working electrode and lithium foil as both counter and reference electrodes with a scan rate of  $5 \text{ mV s}^{-1}$ . CV was performed in  $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  coin cells with a scan rate of  $0.1 \text{ mV s}^{-1}$ . The electrochemical impedance spectroscopy (EIS) measurements were carried out at fully discharged state, the AC perturbation was  $\pm 10 \text{ mV}$ , and the frequency range was from  $10^5 \text{ Hz}$  to  $10^{-1} \text{ Hz}$  on a PGSTAT-302N electrochemical station (Autolab, Metrohm Co., Switzerland).

The cycled cells were disassembled in an Ar-filled glove box, and the cathodes were rinsed with anhydrous DMC to remove residual solvents and  $\text{LiPF}_6$  salt and dried in vacuum at room temperature. The surface morphology was observed with scanning electron spectroscopy (SEM, JEOL-5900). The surface composition was analyzed with X-ray photoelectron spectroscopy (XPS) on ESCALAB 250 using a focused monochromatized Al  $K_{\alpha}$  radiation ( $h\nu = 1486.6 \text{ eV}$ ) under ultra high vacuum. The final adjustment of the energy scale was made based on the C 1s peak of graphite at 284.3 eV. The spectra obtained were fitted using XPSpeak 4.1. Lorentzian and Gaussian functions were used for the least-square curve fitting procedure. The organic functional groups in the surface components were characterized by Fourier transform infrared spectroscopy (FTIR) (Bruker Tensor 27) within  $600\text{--}4000 \text{ cm}^{-1}$ .

The energy levels of the highest occupied molecule orbital (HOMO) of the electrolyte solvents and the additive DMPP were calculated by using Gaussian 03 programs package. The equilibrium and transition structures were fully optimized by B3LYP method at 6-31 + G (d, p) basis set.

## 3. Results and discussion

The use of an electrolyte additive might affect the charge/discharge performance. Fig. 1 presents the charge/discharge profiles of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode with 0.2C rate at room temperature between 3.5 and 4.95 V in the STD electrolytes containing various DMPP concentrations. It can be seen from Fig. 1 that increasing DMPP concentration causes the decrease of charge/discharge efficiency: 92.9, 83.2 and 76.9% for the electrolytes containing 0 and 0.5 and 1% DMPP, respectively. This result suggests that DMPP decomposes on  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  more easily than the STD electrolyte. It can also be noted from Fig. 1 that the discharge capacity is reduced

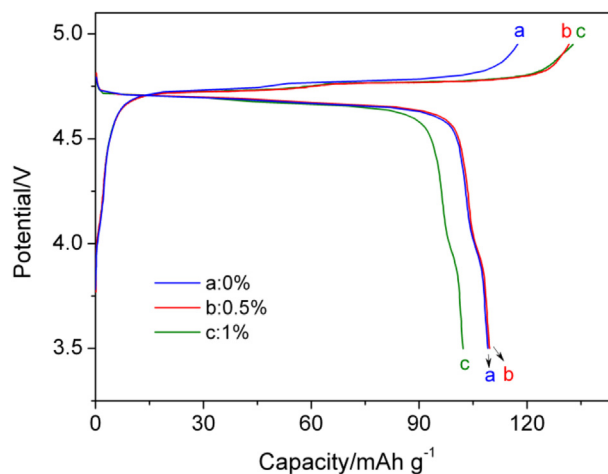


Fig. 1. Charge/discharge profiles of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode with 0.2C at room temperature between 3.5 and 4.95 V in STD electrolytes containing various DMPP concentration.

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