



Short communication

Trimethyl phosphite as an electrolyte additive for high-voltage lithium-ion batteries using lithium-rich layered oxide cathode

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HIGHLIGHTS

- Trimethyl phosphite (TMP) is investigated as a high-voltage electrolyte additive.
- Addition of 1% TMP can enhance capacity retention and rate capability.
- The passivating interphase is built by TMP on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode.

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ABSTRACT

Lithium-rich layered oxide cathode is a promising high-capacity cathode material for high-energy lithium-ion batteries. However, to achieve its high capacity, the development of high-voltage electrolytes is essential. In this work, trimethyl phosphite (TMP) is investigated as an electrolyte additive for high-voltage lithium-ion batteries using $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode. When 1% TMP is introduced into the electrolyte, cycling performance and rate capability of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode are improved significantly. The $\text{Li}/\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cell with the TMP-containing electrolyte exhibits high capacity retention of 81.3% after 100 cycles and good rate capability of 150 mA h g^{-1} at 5 C and 90 mA h g^{-1} at 10 C, while the capacity of the cell without TMP is 48 mA h g^{-1} at 5 C. Based on the measurements on impedance spectra and thermal stability, it is concluded that TMP can effectively deactivate the catalyzing effect of some transition metal ions on the surface of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode.

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1. Introduction

Lithium-rich layered oxide cathode materials, represented by $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Ni}, \text{Co}, \text{Mn}$), have been intensively studied as high capacity cathode materials for lithium-ion batteries [1–10]. They usually can deliver a reversible capacity of $\sim 250 \text{ mA h g}^{-1}$ between 2.0 and 4.8 V, which is quite attractive to high-energy lithium-ion batteries for electric vehicle applications. Such a large capacity cannot be achieved until the cathode is charged to an upper cut-off voltage of 4.6–4.8 V in order to activate Li_2MnO_3 component. The high voltage is a rigorous challenge to the state-of-the-art electrolyte. Although the organic carbonate solvents in the

electrolyte usually have quite high anodic potentials exceeding 5 V on inert electrodes, they seldom keep stable enough at potentials only above 4.4 V during long-term cycling on the active electrode [11]. The main reason is that the carbonate solvents are apt to be catalyzed to decompose by strongly oxidative charged electrode. These aggressive side reactions are responsible for the large initial irreversible capacity loss and distinct capacity fading during cycling.

In order to make lithium-rich layered oxide cathode materials commercially available, it is necessary to improve the stability of electrolyte on these high-voltage cathodes. There are two ways to make the electrolyte compatible with the high-voltage cathodes. One is to replace the carbonate-based electrolytes with novel electrolyte systems intrinsically exhibiting high anodic stability. Succinonitrile and sulfone-based electrolytes have been investigated in the 5 V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells and LiCoO_2 cells with charge cut-off voltage of 4.5 V [12,13]. The other way is to make the

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carbonate-based electrolytes dynamically stable to the high-voltage cathodes. At most time, some additives were used to deactivate the active “catalytic” centers on the cathode surface in order to remain inert for the bulk electrolyte [14–16]. Lucht *et al.* reported that inorganic additives including lithium bisoxalato-borate, lithium difluoro-oxalato-borate and tetramethoxy titanium could effectively passivate the $\text{Li}_{1.17}\text{Mn}_{0.58}\text{Ni}_{0.25}\text{O}_2$ cathode and result in a decrease in detrimental electrolyte oxidative decomposition reactions on the cathode surface [15]. After Xu *et al.* introduced 1% tris(hexafluoro-iso-propyl) phosphate into the carbonate-based electrolyte, the cycling performance of 5 V lithium-ion batteries had been improved evidently [16]. Basically, exploitation of high-voltage electrolyte additives is a greatly promising route in support of the high-energy lithium-ion batteries using the lithium-rich layered oxide cathodes.

Trimethyl phosphite (TMP) has been investigated as an effective electrolyte additive to improve the safety characteristics of lithium-ion batteries in our previous report [17,18]. In this paper, we explored the feasibility of TMP as an electrolyte additive in support of high-voltage lithium-ion batteries using the cathode material $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, which can be rewritten in two-component notation as $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The impact of TMP on cycling performance and rate capability of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode was investigated. Impedance spectra and thermal stability were measured to deduce the effect of TMP on the cathode/electrolyte interphase.

2. Experimental

2.1. Materials preparation and cell assembly

$\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ was prepared by a co-precipitation method, as described previously [19]. As-purchased TMP was purified with a distillation step under vacuum and dried before use over molecular sieves (4 Å). An electrolyte of 1 M LiPF_6 in a mixture of 1:1 (w/w) ethylene carbonate (EC) and diethyl carbonate (DEC) was selected as a baseline electrolyte. Different contents of TMP were added in the baseline electrolyte in an argon-filled glove box (MBraun).

Electrochemical properties of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode material were evaluated by using 2032-type coin cells assembled in the glove box. In order to make the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ electrode laminate, a slurry containing 84 wt.% active material, 8 wt.% acetylene black and 8 wt.% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrrolidinone (NMP) was cast onto an aluminum current collector. After vacuum drying at 70 °C, the laminate was punched into discs (14 mm) for assembling the coin cells. The mass loading in the electrode was controlled at about 8 mg cm^{-2} . Celgard 2400 microporous polypropylene membrane was used as separator. Highly pure lithium foil was used as the counter electrode and reference electrode for the cell assembly.

2.2. Measurements on electrochemical properties and thermal stability

Electrochemical stability of the electrolytes on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ electrodes was measured by linear sweep voltammetry (LSV) from open circuit potential to 6 V at a scan rate of 0.2 mV s^{-1} . Ac impedance measurements were performed over the frequency range of 100 kHz to 1 mHz at an amplitude of 10 mV. Both measurements were carried out in the $\text{Li}/\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cells on a CHI 604D electrochemical workstation. The cell performance of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ was evaluated on a multi-channel battery cycler (Neware BTS2300). All the cells were cycled between 2.5 and 4.8 V at a current rate of 0.1 C (1 C = 200 mA g^{-1}) for the initial three cycles. Then the cycling tests were performed at

a current rate of 0.5 C in the constant current–constant voltage (CC–CV) charge mode and constant current (CC) discharge mode between 2.5 and 4.6 V. The internal resistance of the cells was also measured by a current interruption technique. This was done by cutting off the current intermittently for 1 min through the process of charge and recording the voltage change after interruption. Thus, the dc impedance of a cell (R_{dc}) can be calculated as $R_{dc} = \Delta U/\Delta I$, where ΔU is the difference between the voltage of before and after the 1-min interruption [20]. All the testing above was performed in room temperature.

Thermal stability of the coexisting systems of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode and electrolyte was evaluated by using a Calvet-type calorimeter (Setaram C80). 23 mg cathode material and 50 mg electrolyte were placed in a high-pressure stainless steel vessel with dry argon atmosphere. The measurement was performed at a heating rate of 0.2 °C min^{-1} from room temperature to 300 °C, and the C80 calculations were based on the weight of the electrolyte. More details can be found in our previous report [21].

2.3. Calculation details

Based on Faraday's law, the oxidation potential of TMP vs. Li/Li^+ can be calculated from the following formula:

$$E_0 = -[G_0(\text{TMP}) - G_0(\text{TMP}^+)]/e - 1.46 \text{ V} \quad (1)$$

The calculation of TMP's oxidation potential was performed by using the Gaussian03 program package [22]. The structures of TMP and TMP^+ were fully optimized by B3LYP method using 6-311++G(d,p) basis set. The polarizable continuum model (PCM) model was used in our calculations, since it can produce reasonable results in describing solvation effects on redox potentials in the electrolyte. Herein, the solvent radius is fixed to be 5.0 Å and dielectric constant to be 60.0 as reported by Dahn [23].

3. Results and discussion

In the TMP molecule, the oxidation number of phosphorous is three (III) and the phosphorous atom has a lone pair. Along with one electron lost, TMP can be oxidized into TMP^+ . After the TMP and TMP^+ structures were fully optimized, their standard free energies were calculated. Based on formula (1), the oxidation potential of TMP was calculated to be 4.93 V, which is lower than the oxidation potentials of EC and DEC. Therefore, TMP should be preferential to oxidize on the charged $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ than EC and DEC.

Fig. 1 shows the LSV curves of the electrolyte with or without 1% TMP on the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ electrode. Both the curves contain three anodic peaks at 4.0 V, 4.6 V and 5.3 V, respectively. The first peak at 4.0 V is associated predominantly with Ni oxidation from Ni^{2+} to Ni^{4+} and Co oxidation from Co^{3+} to Co^{4+} , and the peak at 4.6 V is related to the electrochemical activation reaction of Li_2MnO_3 to MnO_2 with Li_2O stripped [24,25]. The last peak at 5.3 V is quite weak, which is resulted from the oxidation of the electrolyte on the high-voltage electrode. There is negligible difference between the two curves when the voltage is below 4.9 V. However, at the high potential region, the onset oxidative potential of the electrolyte with TMP is about 4.9 V, which is lower than 5.1 V of the baseline electrolyte. Moreover, the oxidative peak of the electrolyte with TMP is higher and broader than that of the electrolyte without TMP. The possible reason is that TMP is apt to oxidative decomposition in a more aggressive way. The onset oxidative potential of TMP is about 4.9 V, which is in good agreement with the calculation result (4.93 V).

The cell performance of $\text{Li}/\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cells containing the electrolytes with and without TMP is shown in Fig. 2. All

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