Tris (pentafluorophenyl) phosphine: An electrolyte additive for high voltage Li-ion batteries

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A B S T R A C T

Tris (pentafluorophenyl) phosphine (TPFPP) is used as an electrolyte additive to improve the cycling performance of high voltage (~5 V) lithium-ion battery. The electrochemical behaviors and surface chemistry of LiNi0.5Mn1.5O4 are investigated via cyclic voltammetry, chronoamperometry, charge–discharge test, X-ray photoelectron spectroscopy, and theoretical computations. It is found that the cycling performance of the cell Li/LiNi0.5Mn1.5O4 using an electrolyte of 1.0 M LiPF6 in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1/1/1, in volume), can be improved by adding TPFPP into the electrolyte. The theoretical calculations predict that TPFPP is preferably oxidized compared to the solvents. Electrochemical measurements and XPS analyses show that a protective film is formed on LiNi0.5Mn1.5O4 when TPFPP is used, which contributes to the cycling performance improvement of the cell.

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1. Introduction

Lithium ion battery has been widely used for portable electronics and is believed to be a promising power source for electric vehicles [1]. Its energy density needs to be improved for the application in electric vehicles, and thus many efforts have been focused on the increase in its operating voltage by using high voltage cathode materials such as LiNi0.5Mn1.5O4 (4.9 V vs. Li/Li⁺) [2–4]. However, cycling of lithium-ion cells to high voltages (> 4.5 V vs. Li/Li⁺) is always accompanied by the significant oxidative decomposition of the conventional carbonate/LiPF6 electrolyte, resulting in relatively low coulombic efficiency and poor cycling performance [5,6].

Various procedures have been proposed to inhibit the detrimental reactions on high voltage cathode materials, including surface coating by using various inorganic oxides [7,8], and application of novel solvents or additives [2,3,9,10]. The surface-coating improves the cyclability but reduces the discharge capacity of the high voltage materials. Several solvents, such as lactone and sulfone, were reported to be stable at 5 V (vs. Li/Li⁺), but most of them have high viscosity or do not favor the formation of a protective solid electrolyte interphase (SEI) on graphite anode.

Phosphine-based compounds were previously reported as flame-retardant additives for lithium ion battery due to the ability of radical-scavenging for the combustion reactions [11,12]. In this study, we reported a phosphine-based compound, tris (pentafluorophenyl) phosphine (TPFPP), as a novel additive of electrolyte for cyclability improvement of the high voltage lithium ion battery with LiNi0.5Mn1.5O4 as cathode.

2. Experiment

The blank electrolyte (STD), 1.0 M LiPF6 in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1/1/1, in volume), was provided by Guangzhou Tinci Materials Technology Co. Ltd, China. The additive, tris (pentafluorophenyl) phosphine (TPFPP), was purchased from Strem Chemicals, Inc. (USA) and used without further purification. The LiNi0.5Mn1.5O4 electrode was prepared by mixing the mixture of 89 wt.% LiNi0.5Mn1.5O4 (Shanshan Advanced Material Co., China), 6 wt.% acetylene carbon black and 5 wt.% PVDF binder, coating on Al foil.

Electrochemical behaviors of LiNi0.5Mn1.5O4 electrode in the electrolytes with and without TPFPP were determined by cyclic voltammetry (CV) and chronocoulometry on Solartron-1480 instrument (England). The scan rate of CV was 50 μV s⁻¹.

Coin cells were fabricated with LiNi0.5Mn1.5O4 electrode as the positive, lithium foil as the negative and Celgard 2025 as the separator. The cells were cycled at room temperature, charged at constant-current and then under constant-voltage and discharged at constant-current on LAND test system (CT2001A, China).

The chemical analyses of Mn and Ni contents in the electrolyte were performed by inductive coupled plasma (ICP) spectroscopy (Thermo, USA). All calculations are performed on Gaussian 03
The disassembled LiNi0.5Mn1.5O4 cathodes were washed with anhydrous DMC solvent 3 times to remove residual EC and LiPF6 salt followed by vacuum drying overnight at room temperature. The XPS was conducted on ESCALAB 250, using a focused monochromatized Al Kα radiation (\(h\nu = 1486.6\) eV). The graphite peak at 284.3 eV was used as a reference for the final adjustment of the energy scale in the spectra. The spectra obtained were fitted using XPS peak software (version 4.1). Line syntheses of elemental spectra were conducted using a Gaussian–Lorentzian (80:20) curve fit with Shirley background subtraction.

3. Results and discussion

3.1. Cycling performance of LiNi0.5Mn1.5O4 cells

Fig. 1 shows cyclic performances of Li/LiNi0.5Mn1.5O4 cells. Comparing the cell using 0.5% TPFPP with the cell without TPFPP at 0.2 C rate. It can be seen that the use of TPFPP significantly improves the cycling performance of the cell. The cell without using the additive experiences a capacity drop from 121.9 mAh g\(^{-1}\) to 85.7 mAh g\(^{-1}\), with the capacity retention of 70.3% after 55 cycles, while capacity of the cell with the additive at 55th cycle is 106.9 mAh g\(^{-1}\) and retains 85.0% of its initial capacity (125.8 mAh g\(^{-1}\)). However, when increasing the discharge rate, the capacity of the cell fades dramatically, although the cell using 0.5% TPFPP shows better performance than the cell without TPFPP. This is caused by the poor conductivity of LiNi0.5Mn1.5O4, which can be improved by carbon coating. It should be noted that the cell using 1% TPFPP shows poorer cycling stability than the cell using 0.5% TPFPP, suggesting that TPFPP as an additive can only be used in a small concentration.

To understand the effect of TPFPP, cyclic voltammetry and chronocoulometry were performed on LiNi0.5Mn1.5O4 electrode, and the surface chemistry of the LiNi0.5Mn1.5O4 obtained from the cycled cells was identified with XPS.

3.2. Electrochemical behaviors of LiNi0.5Mn1.5O4 electrode

Fig. 2a shows the cyclic voltammograms of LiNi0.5Mn1.5O4 electrode in the electrolyte with and without TPFPP. One pair of redox peaks between 4.5 and 4.9 V corresponding to the oxidation/reduction of nickel can be observed for both electrolytes during the first cycle and consecutive cycles. The LiNi0.5Mn1.5O4 electrode in the TPFPP containing electrolyte shows better reversibility of lithium-removal/insertion than that in the electrolyte without additive, since there is lower hysteresis between de-intercalation/intercalation process in the TPFPP containing electrolyte, which offers a higher coulombic efficiency and faster kinetics [13].

Fig. 2b shows the chronocoulometric and chronoamperometric responses of the LiNi0.5Mn1.5O4 electrode in the electrolytes with and without TPFPP at 5.2 V. The LiNi0.5Mn1.5O4 electrode in the electrolyte without additive has larger residual current than that in the TPFPP containing electrolyte, suggesting that the electrolyte without TPFPP is subjected to oxidative decomposition more easily than the TPFPP containing electrolyte.

3.3. Preferable oxidative decomposition of TPFPP

The oxidative stability of TPFPP was understood by DFT calculations with a comparison of solvents, EC, DMC and DEC. The equilibrium state structures of EC, DMC, DEC, TPFPP, and their radical cations were optimized by B3LYP method at 6–311++G(d,p) basis set. The Gibbs free energy (\(\Delta G\)) between the neutral molecules and their radical cations is 1019.7 (803.7), 993.4 (872.0), 959.1 (841.1), and 819.7 (638.6) kJ mol\(^{-1}\) for EC, DMC, DEC, and TPFPP in gas and solution (in bracket), respectively, suggesting that the solvents and TPFPP in electrolyte is stable under nonpolarization. However, the \(\Delta G\) between TPFPP and its oxidative radical cation is much lower than that between the solvents and their oxidative radical cations, indicating that TPFPP is preferential to oxidize on the charged LiNi0.5Mn1.5O4 than DMC, DEC and EC. The HOMO energy of DEC, DMC, and TPFPP (−8.46, −8.21, −8.05, and −7.54 eV, respectively) also indicates the preferable oxidative decomposition of TPFPP.
decomposition of TPFPP. The computation results are in good agreement with the modified electrochemical behaviors as discussed above.

3.4. Surface chemistry of LiNi$_0.5$Mn$_{1.5}$O$_4$

Fig. 3 presents the XPS patterns of LiNi$_0.5$Mn$_{1.5}$O$_4$ electrodes from the cycled cells, with a comparison of the fresh LiNi$_0.5$Mn$_{1.5}$O$_4$ electrode. The element concentrations obtained from XPS analyses are presented in Table 1. It can be seen from Fig. 3 that new species corresponding to the electrolyte decomposition products are detected on the cycled electrode surface and there is a significant difference in XPS patterns between the electrodes cycled in the electrolytes with and without TPFPP. Besides the peaks appearing in the fresh electrode, there appear the peaks corresponding to C–O (−286 eV) and C=O (−288 eV) containing species in the C 1s spectra of the cycled LiNi$_0.5$Mn$_{1.5}$O$_4$ electrodes. However, the intensities of C–O and C=O containing species present on the cycled electrode in TPFPP containing electrolyte are slightly stronger than those of the cycled electrode in the electrolyte without TPFPP. This indicates that the cycled electrode in the TPFPP containing electrolyte is slightly more protected than that in the electrolyte without additive. As shown in Table 1, the C 1s concentration is 52.7% for the cycled electrode in the TPFPP containing electrolyte but 38.3% for the cycled electrode in the electrolyte without additive.

In addition, the intensities of C–O (533.7 eV) and M–O (529.5 eV) peaks in O 1s of the cycled electrode in the TPFPP containing electrolyte are much stronger than those of the cycled electrode in the electrolyte without additive. The results suggest that more protective film or SEI is formed with the incorporation of the oxidative decomposition products of TPFPP on the cycled electrode in the TPFPP containing electrolyte than in the electrolyte without additive.

Significant differences in F 1s spectra are observed for both cycled electrodes. The cycled electrode in the electrolyte without additive has the peaks for LiF (684.5 eV) and the peak for Li$_x$PO$_y$F$_z$ (686.8 eV) and PVDF, while the cycled electrode in the TPFPP containing electrolyte has only the peaks for Li$_x$PO$_y$F$_z$ (686.8 eV) and PVDF, suggesting that the F 1s of both cycled electrodes comes from different sources. Based on the composition of the electrolytes, the F 1s can be ascribed to the additive TPFPP for the cycled electrode in the TPFPP containing electrolyte and the salt LiPF$_6$ for the cycled electrode in the electrolyte without additive, except for PVDF binder. As shown in Table 1, the concentration of F 1s on the cycled electrode in the TPFPP containing electrolyte is larger than that on the cycled electrode in the electrolyte without additive. Similar phenomena appear in sources of P 2p. Although the concentration of P 2p is the same for both cycled electrodes (Table 1), the contribution of LiPF$_6$ (137.8 eV) to the P 2p can be observed on the cycled electrode in the electrolyte without additive but not on the cycled electrode in the TPFPP containing electrolyte, as shown in Fig. 3. The lithium electrodes from the cycled cells were washed with DMC solvent after cycling and then analyzed with ICP-MS. The content of Mn and Ni is 638 and 11 ppb for the electrolyte without additive while 199 and 10 ppb for the TPFPP containing electrolyte, respectively, indicating that the metal elements in LiNi$_0.5$Mn$_{1.5}$O$_4$ is easier to dissolve in the electrolyte without additive. These results confirm that TPFPP helps form a protective film or SEI on LiNi$_0.5$Mn$_{1.5}$O$_4$ which prevents electrolytes and LiNi$_0.5$Mn$_{1.5}$O$_4$ from oxidative decomposition and improves the cycling performance of the cell using LiNi$_0.5$Mn$_{1.5}$O$_4$ as cathode.

### Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>C 1s (%)</th>
<th>O 1s (%)</th>
<th>F 1s (%)</th>
<th>P 2p (%)</th>
<th>Ni 2p (%)</th>
<th>Mn 2p (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>58.1</td>
<td>16.7</td>
<td>14.7</td>
<td>3.3</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>STD</td>
<td>38.3</td>
<td>40.8</td>
<td>19.2</td>
<td>1.3</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>STD + 0.5% TPFPP</td>
<td>52.7</td>
<td>18.4</td>
<td>22.2</td>
<td>1.3</td>
<td>2.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Fig. 3. XPS patterns of fresh LiNi$_0.5$Mn$_{1.5}$O$_4$ electrode (fresh) and cycled LiNi$_0.5$Mn$_{1.5}$O$_4$ electrodes in blank electrolyte (STD) and TPFPP containing electrolyte (STD + 0.5% TPFPP). The cycled electrodes were taken from the Li/LiNi$_0.5$Mn$_{1.5}$O$_4$ cells after 55 cycles.
4. Conclusions

Tris (pentafluorophenyl) phosphine (TPFPP) can be used as an electrolyte additive for cycling performance improvement of high voltage (~5 V) lithium ion battery. It can be preferably oxidized on cathode of a charged lithium ion battery compared to solvents, forming a protective film or an SEI on the cathode, which prevents electrolytes and cathode materials from oxidative decomposition and thus improves the cycling performance improvement of lithium ion battery.

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