Supporting Information

Diethyl (thiophen-2-ylmethyl) phosphonate: A Novel Multifunctional Electrolyte Additive for High Voltage Batteries

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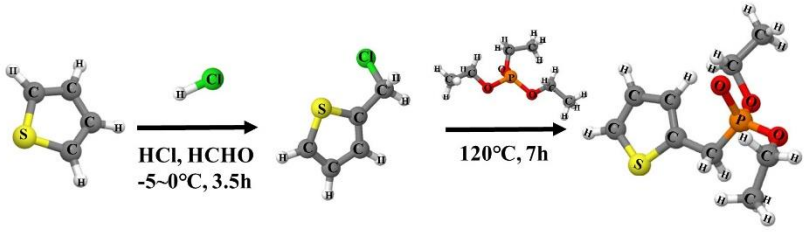
Captions:

Scheme S1. Synthesis path of diethyl (thiophen-2-ylmethyl) phosphonate (DTYP).
Figure S1. ^{1}H NMR spectra of diethyl (thiophen-2-ylmethyl) phosphonate (DTYP) in TMS.
Table S1. Parameters from GC-MS of DTYP.
Figure S2. Rate capability of $LiNi_{0.5}Mn_{1.5}O_4$ electrodes in base and DTYP-containing electrolytes under room temperature.
Figure S3. Cyclic stabiliy (A) and Coulombic efficiency (B) of $LiNi_{0.5}Mn_{1.5}O_4$ electrodes in the electrolytes containing various contents of DTYP under room temperature at 0.5 C for the first three cycles and at 1 C for the subsequent cycles between 3 V and 4.9 V, followed by a constant potential of 4.9 V until the current reaches 0.1 C.
Figure S4. Cyclic stability (A) of $LiNi_{0.5}Mn_{1.5}O_4$/graphite full cells with and without DTYP at 0.1 C for the activation and at 0.2 C for the follow cycles from 3.0~4.9 V, followed by a constant potential for current below 0.01 and 0.02 C; Charge/discharge profiles of the selected cycles in electrolytes without (B) and with (C) DTYP; (D) Mean charge/discharge voltages of the selected cycles in base and DTYP-containing electrolytes.
Figure S5. Cyclic stability and Coulombic efficiency of graphite electrodes in electrolytes with and without 0.5% DTYP under room temperature at 0.2 C between 0.005V and 2.5 V.
Figure S6. SEM images from different position angles under different resolutions from Fig. 2A for pristine (A) and the cycled $LiNi_{0.5}Mn_{1.5}O_4$ electrodes in base (B) and DTYP-containing (C) electrolytes.
Table S2. Contents of Ni, Mn and Al that deposit on the lithium electrode after cycling in base and DTYP-containing electrolytes.
Figure S7. Photos of puncture experiments for pouch batteries with base and DTYP-containing electrolytes.



Scheme S1. Synthesis path of diethyl (thiophen-2-ylmethyl) phosphonate (DTYP).

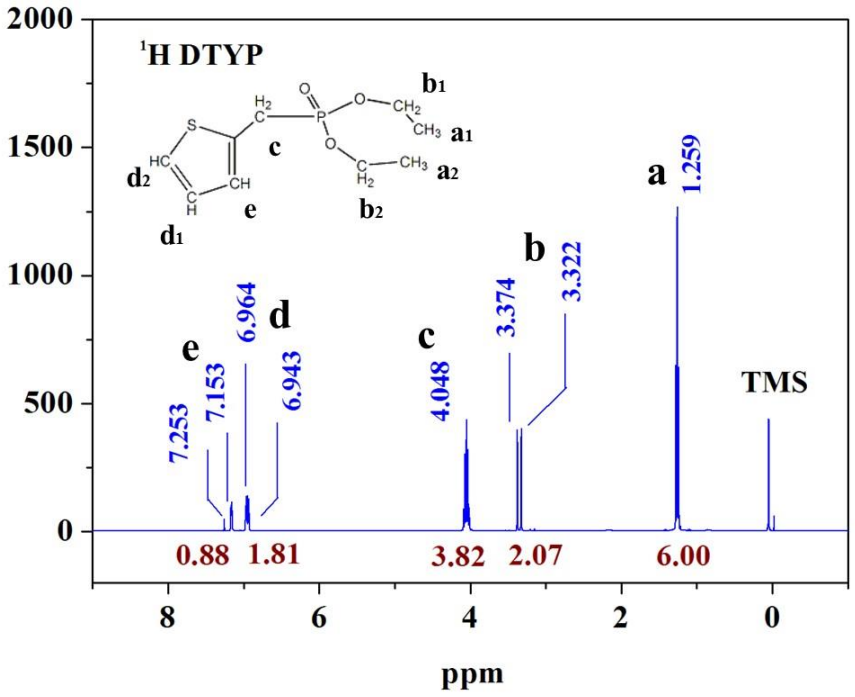


Figure S1. ^{1}H NMR spectra of diethyl (thiophen-2-ylmethyl) phosphonate (DTYP) in TMS.

Table S1. Parameters from GC-MS of DTYP.

Retention time	Peak area	Peak high	Concentration
2.673	**13188**	**7728**	**0.039**
4.687	**2244**	**1262**	**0.007**
6.874	**16428**	**7776**	**0.048**
7.502	**2420**	**1285**	**0.007**
12.015	**46181**	**24122**	**0.136**
12.110	**7418**	**3697**	**0.022**
13.313	**33814308**	**3144408**	**99.254**
13.703	**101130**	**43279**	**0.297**
14.280	**12732**	**6421**	**0.037**
14.387	**17570**	**8449**	**0.052**
14.652	**22632**	**10777**	**0.066**
14.877	**3700**	**1266**	**0.011**
15.370	**5156**	**2745**	**0.015**
15.602	**3263**	**1777**	**0.010**

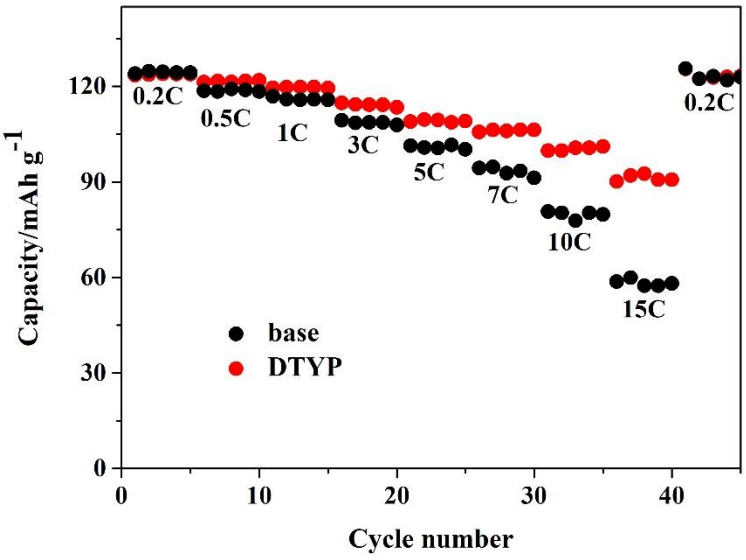


Figure S2. Rate capability of $LiNi_{0.5}Mn_{1.5}O_4$ electrodes in base and DTYP-containing electrolytes under room temperature.

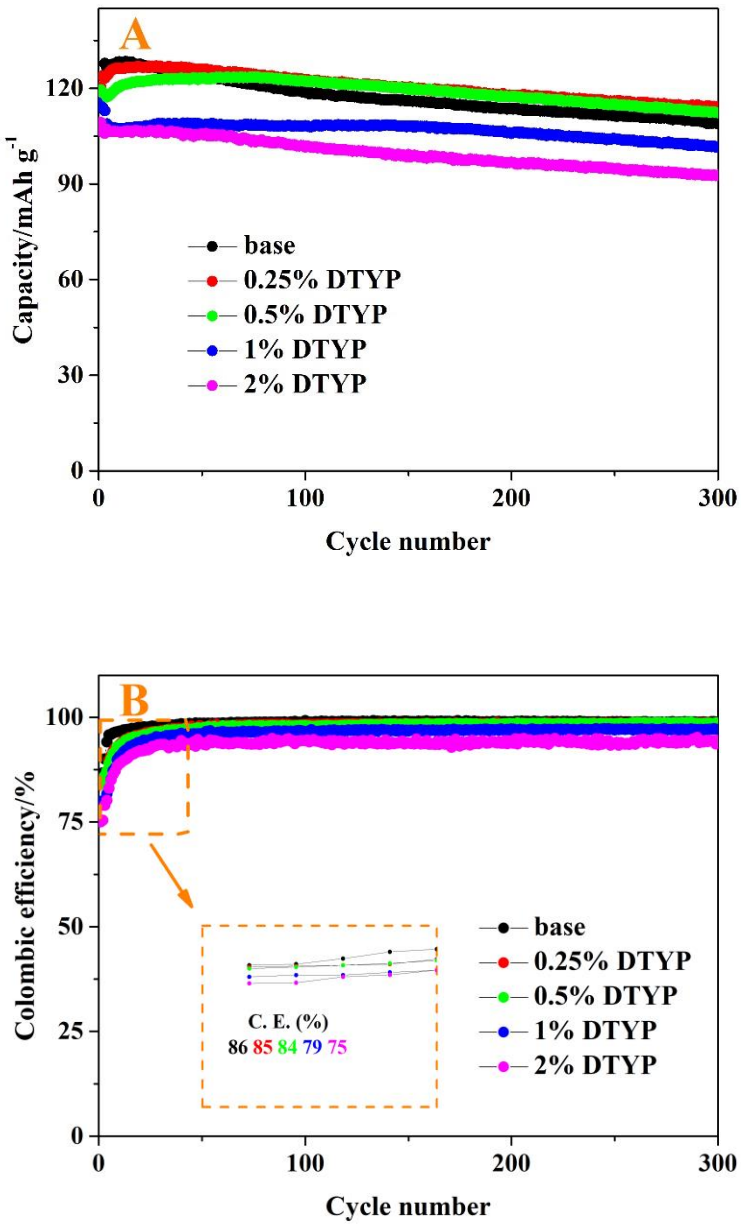


Figure S3. Cyclic stability (A) and Coulombic efficiency (B) of $LiNi_{0.5}Mn_{1.5}O_4$ electrodes in the electrolytes containing various contents of DTYP under room temperature at 0.5 C for the first three cycles and at 1 C for the subsequent cycles between 3 V and 4.9 V, followed by a constant potential of 4.9 V until the current reaches 0.1 C.

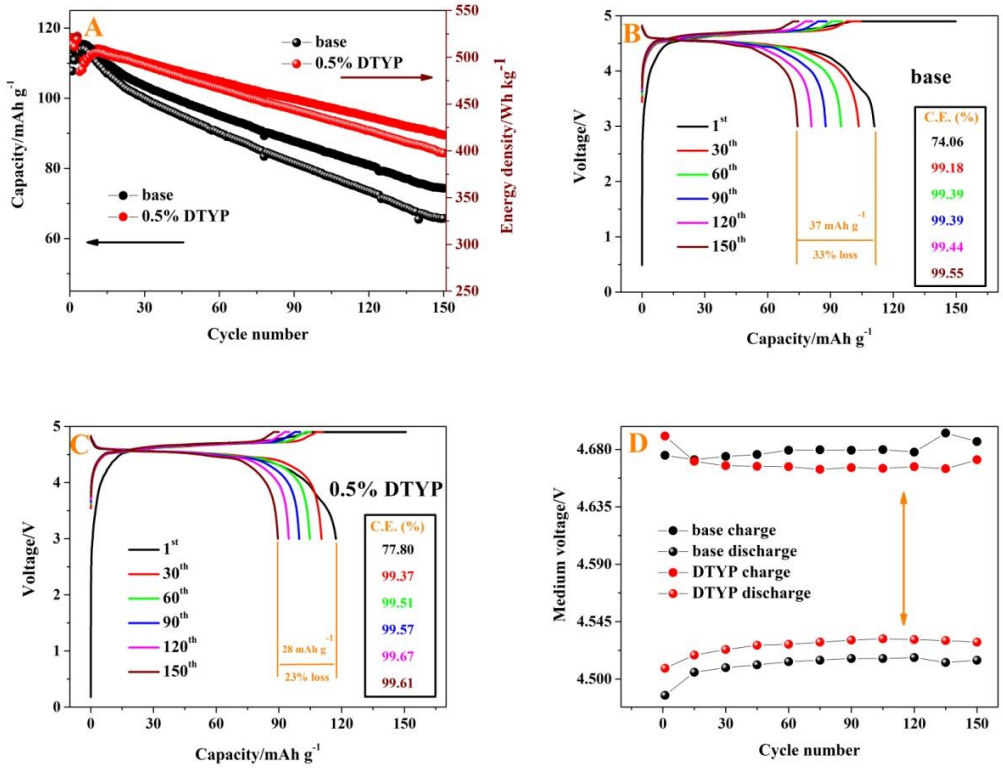


Figure S4. Cyclic stability (A) of $LiNi_{0.5}Mn_{1.5}O_4$/graphite full cells with and without DTYP at 0.1 C for the activation and at 0.2 C for the follow cycles from 3.0~4.9 V, followed by a constant potential for current below 0.01 and 0.02 C; Charge/discharge profiles of the selected cycles in electrolytes without (B) and with (C) DTYP; (D) Mean charge/discharge voltages of the selected cycles in base and DTYP-containing electrolytes.

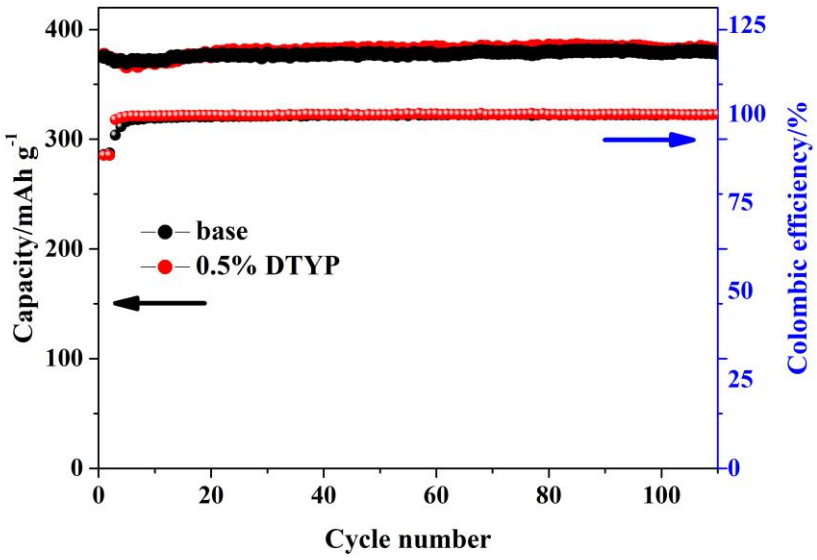


Figure S5. Cyclic stability and Coulombic efficiency of graphite electrodes in electrolytes with and without 0.5% DTYP under room temperature at 0.2 C between 0.005V and 2.5 V.

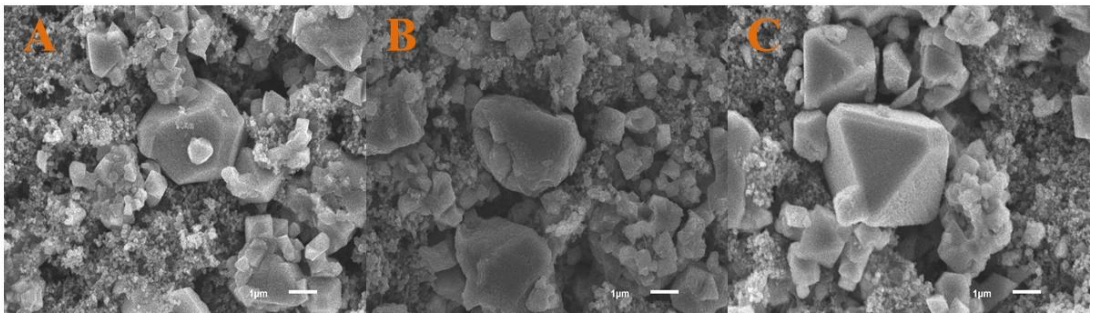


Figure S6. SEM images from different position angles under different resolutions from Figure 2A for pristine (A) and the cycled $LiNi_{0.5}Mn_{1.5}O_4$ electrodes in base (B) and DTYP-containing (C) electrolytes.

Table S2. Contents of Ni, Mn and Al that deposit on the lithium electrode after cycling in base and DTYP-containing electrolytes.

	Ni (mg L^{-1})	Mn (mg L^{-1})	Al (mg L^{-1})
base	**2.18**	**3.61**	**0.57**
DTYP-containing	**0.28**	**0.46**	**0.081**

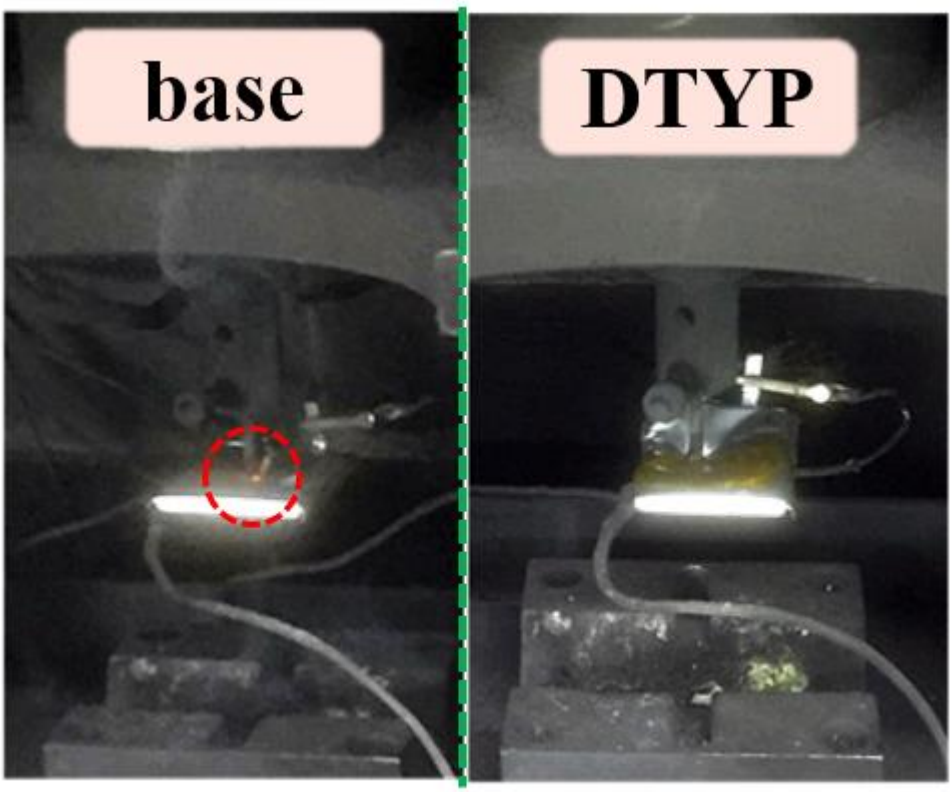


Figure S7. Photos of puncture experiments for pouch batteries with base and DTYP-containing electrolytes.