Supporting Information

Hexamethylene Diisocyanate as an Electrolyte Additive for High-energy density Lithium Ion Batteries

1. Experimental Section

Hexamethylene Diisocyanate(99 %, Aldrich) and carbonate esters (99.5 %, Zhangjiagang Guotai-Huarong New Chemical Materials Co. Ltd.) were mixed in various volume ratios, and a concentration of 1 M $LiPF_6$(Aldrich) was added in an argon-filled glovebox with the H_2O and O_2 content below 1 ppm. 1 M $LiPF_6$ dissolved in PC + DMC(1:1, v/v) was used as the reference electrolyte.

80 wt% $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$(3M, 0.41 m^2 g^{-1}), 10 wt% Super P and 10 wt% PVdF binder were mixed in NMP for cathodes. The mixture was spread onto an aluminum foil current collector and dried. A cell was constructed with a cathode(disk, Ø 14 mm, with 3.5 ~ 4 mg $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ loaded), a glass fiber separator(Whatman), a lithium foil anode and the prepared electrolyte(70 μL) in the same argon-filled glovebox. To investigate the surface reaction, the cathodes were taken from the cells after electrochemical test in an argon-filled glove box, washed with DMC, wiped and vacuum dried overnight in a small chamber of glove box.

Line sweep voltammetry(LSV) was performed on an electrochemical workstation(CHI600D, Shanghai Chenhua Company) at a scan rate of 0.1 mV s^{-1}. Both polarization and charge-discharge test were carried out on a Land cell tester(CT2001A, Wuhan Jinnuo Company) at 25 ℃. The cells were charged up to 4.6 V(*vs.* Li/Li^+) with a constant current (50 μA for Al foils and 0.66 C for $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes) then kept at the potential for 3 h in polarizing, and cycled between 2.5 - 4.6 V(*vs.* Li/Li^+).

Surface analysis was conducted with a PHI 3056 X-ray Photoelectron Spectroscopy(XPS) which was excited by an Mg Ka radiation at a constant power of 100W(15 kV and 6.67 mA), analyzed with GASA, and a PC-controlled Nicolet 6700(Thermo Fisher Scientific). Fourier transform infrared(FTIR) from 600 to 3200 cm^{-1} with a resolution of 0.02 cm^{-1} when the powders of the cathodes were pressed to pellets with KBr. The morphologies of samples were observed with scanning electron microscopy(SEM, HitachiS-4800) and microstructures were examined by transmission electron microscopy(TEM) on a FEI Tecnai F20 equipped with a field emission gun at an accelerating voltage of 200 kV. The electrode resistances were measured on a semiconductor parameter analyzer (Keithley 4200 SCS) at room temperature in the dark with a relative humidity (RH) of 50 %. Two tungsten probes contact bottom aluminum foil and the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ respectively. X-ray diffraction (XRD) was performed on a Bruker D8 Advanced diffractometer with Cu Kα(λ = 1.5406 Å) radiation. The samples were scanned from 10 ° to 90 ° with the step of 0.2 ° and the step duration of 0.2 s.

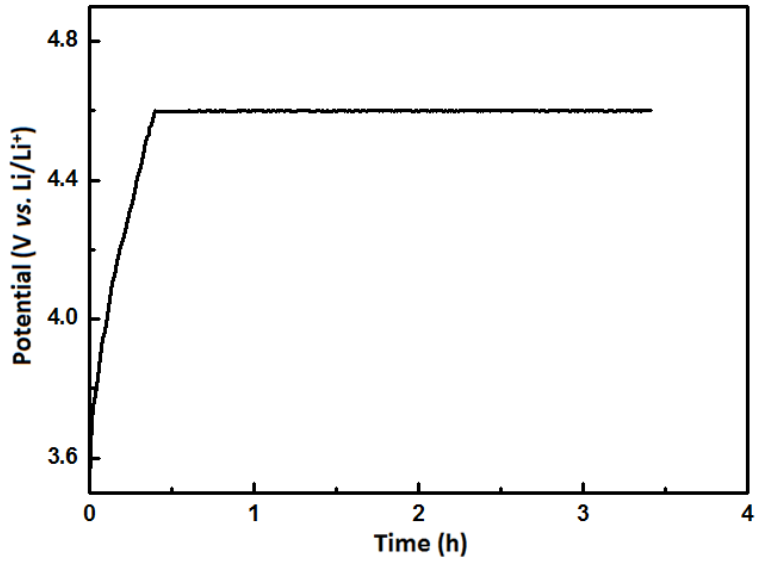
2. Table S1. The initial discharge potentials(V *vs.* Li/Li^+) of cells in PC + DMC(1:1, v/v) 1 M $LiPF_6$ with different concentrations of HDI during cycling at 0.5 C between 2.5 - 4.6 V(*vs.* Li/Li^+).

Cycle number		**1**	**50**	**100**	**150**	**200**
HDI	0 mM	4.5619	4.4798	4.4606	4.4559	4.4420
	1 mM	4.5683	4.5216	4.5201	4.5195	4.5145
	5 mM	4.5624	4.5231	4.5063	4.4959	4.4881
	25 mM	4.5656	4.4819	4.4804	4.4792	4.4723
	100 mM	4.5675	4.3731	4.2897	4.2439	4.1871

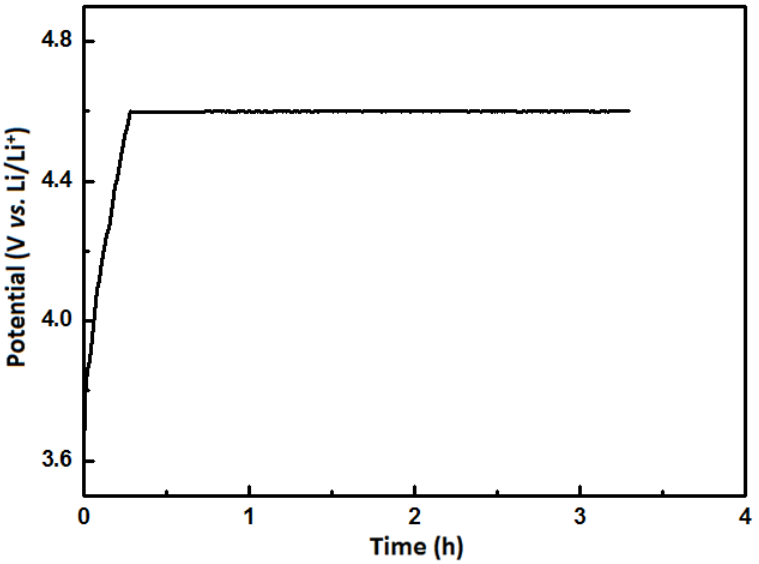
3. Table S2. The mid-potentials(V *vs*. Li/Li^+) of cells in PC + DMC(1:1, v/v) 1 M $LiPF_6$ with different concentrations of HDI during cycling at 0.5 C between 2.5 - 4.6 V(*vs.* Li/Li^+).

Cycle number		**1**	**50**	**100**	**150**	**200**
0 mM	charge	3.9082	3.9418	3.9605	3.9853	4.0089
	discharge	3.8262	3.7936	3.796	3.7666	3.6584
	Δ(charge/discharge)	0.082	0.1482	0.1645	0.2187	0.3505
1 mM	charge	3.9025	3.9274	3.954	3.9682	3.9873
	discharge	3.858	3.8256	3.8057	3.7877	3.7772
	Δ(charge/discharge)	0.0445	0.1018	0.1483	0.1805	0.2101
5 mM	charge	3.9024	3.9234	3.9721	3.9963	4.0283
	discharge	3.8446	3.8259	3.7933	3.7696	3.7459
	Δ(charge/discharge)	0.0578	0.0975	0.1788	0.2267	0.2824
25 mM	charge	3.9066	3.9252	3.9918	4.0707	4.1172
	discharge	3.8379	3.8326	3.7865	3.7615	3.755
	Δ(charge/discharge)	0.0687	0.0926	0.2053	0.3092	0.3622
100 mM	charge	3.9049	4.0443	4.0916	4.2109	4.3328
	discharge	3.8494	3.7391	3.6324	3.4038	3.2388
	Δ(charge/discharge)	0.0555	0.3052	0.4592	0.8071	1.094

4. Figure S1. The charge curves of cells in different electrolytes at 4.6 V(*vs*. Li/Li^+) for 3 h.

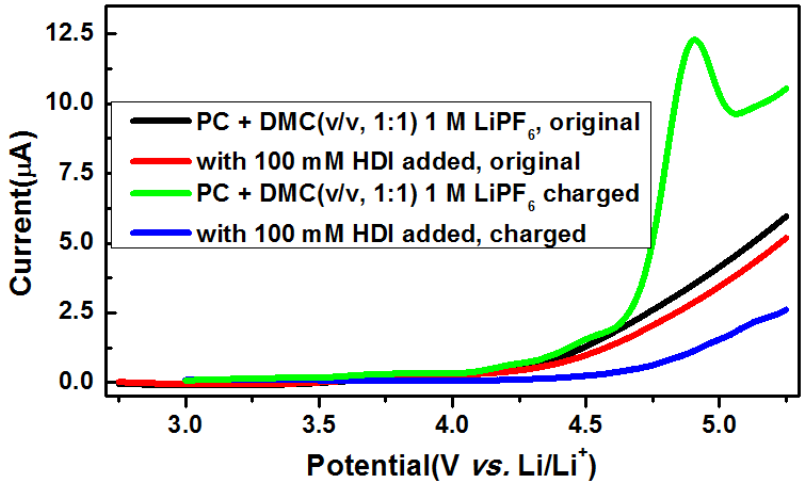


a) The charge curve of a cell with a Al-foil cathode in PC + DMC(1:1, v/v) 1 M $LiPF_6$. The cell was charged at 50 μA to 4.6 V(*vs*. Li/Li^+) and kept at 4.6 V(*vs*. Li/Li^+) for 3 h.

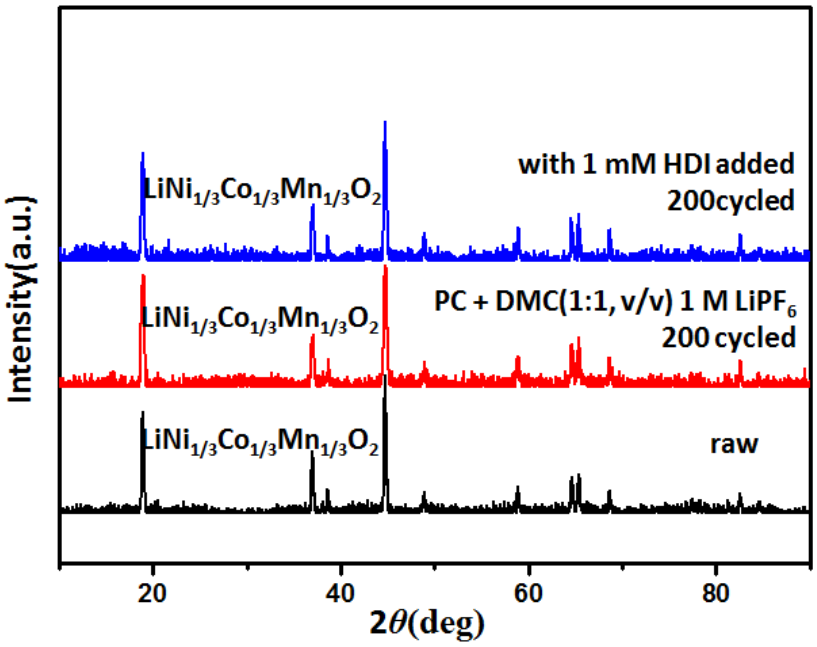


b) The charge curve of a cell with a Al-foil cathode in PC + DMC(1:1, v/v) 1 M $LiPF_6$ with 100 mM HDI added. The cell was charged at 50 μA to 4.6 V(*vs*. Li/Li^+) and kept at 4.6 V(*vs*. Li/Li^+) for 3 h.

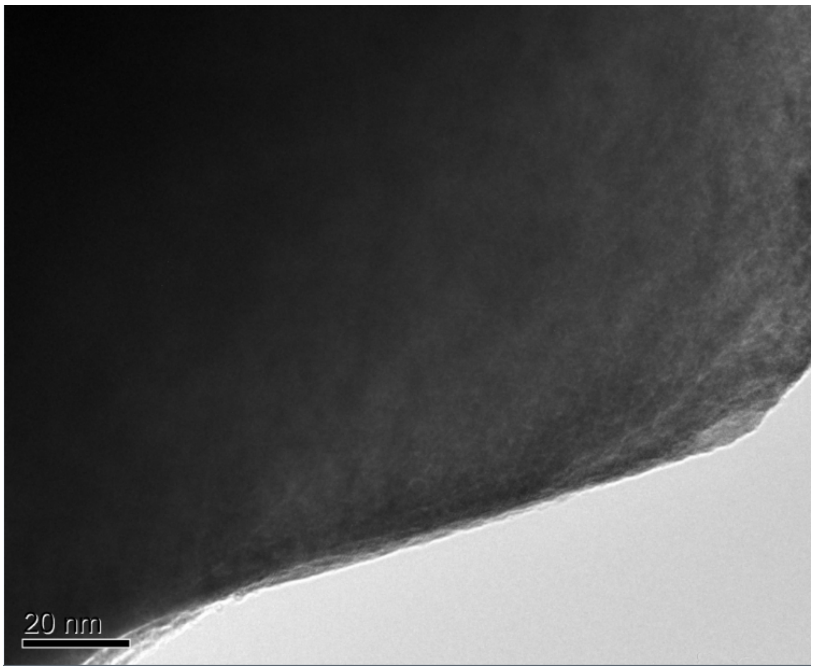
5. Figure S2. LSV curves of the cells in electrolytes with or without 100 mM HDI addition. Scan rate: 0.1 mV s^{-1}.



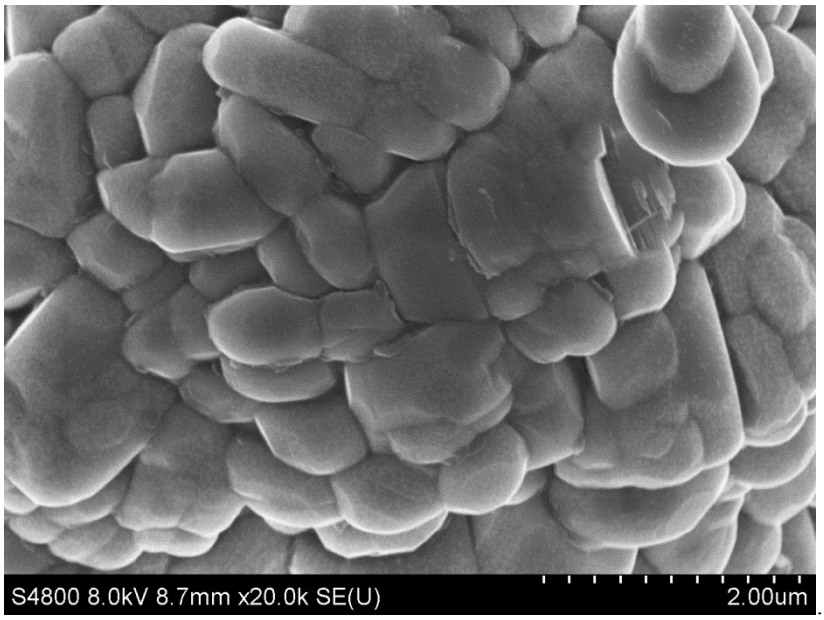
6. Figure S3. XRD patterns of the cathodes in electrolytes with or without 100 mM HDI addition cycled between 2.5 - 4.6 V(*vs.* Li/Li^+).



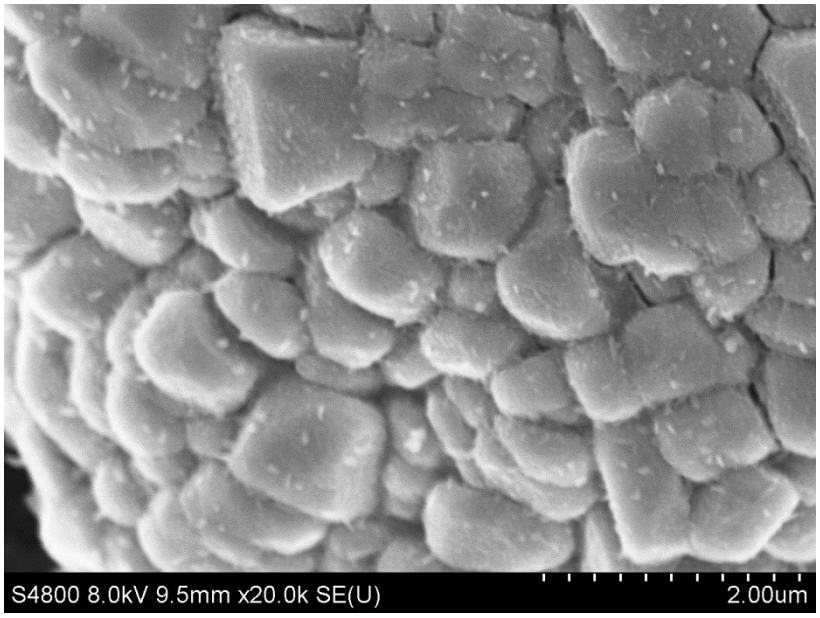
7. Figure S4. TEM image of the cathode surface after soaking in reference electrolyte with 500 mM HDI added for 3 h.



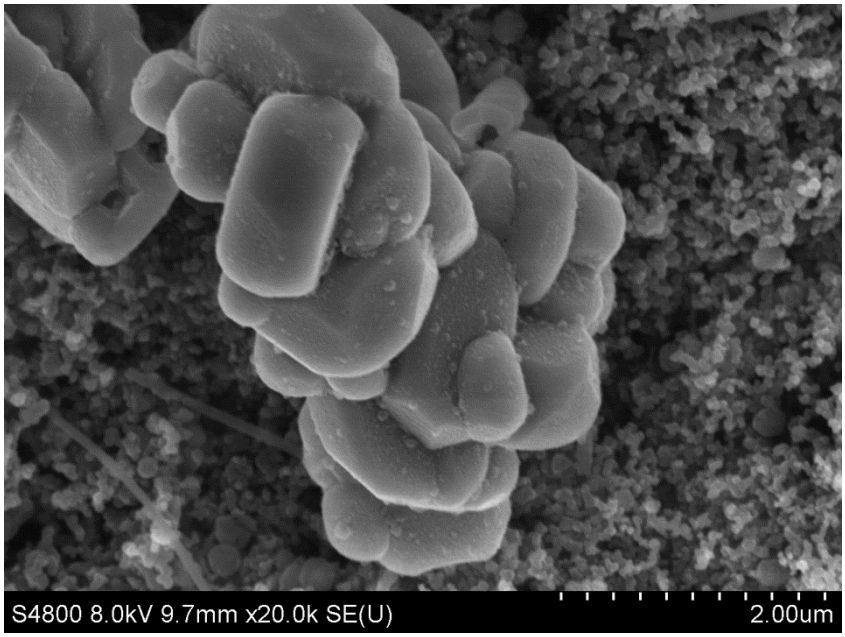
8. Figure S5. Full size SEM images of the cathode surfaces before and after cycled.



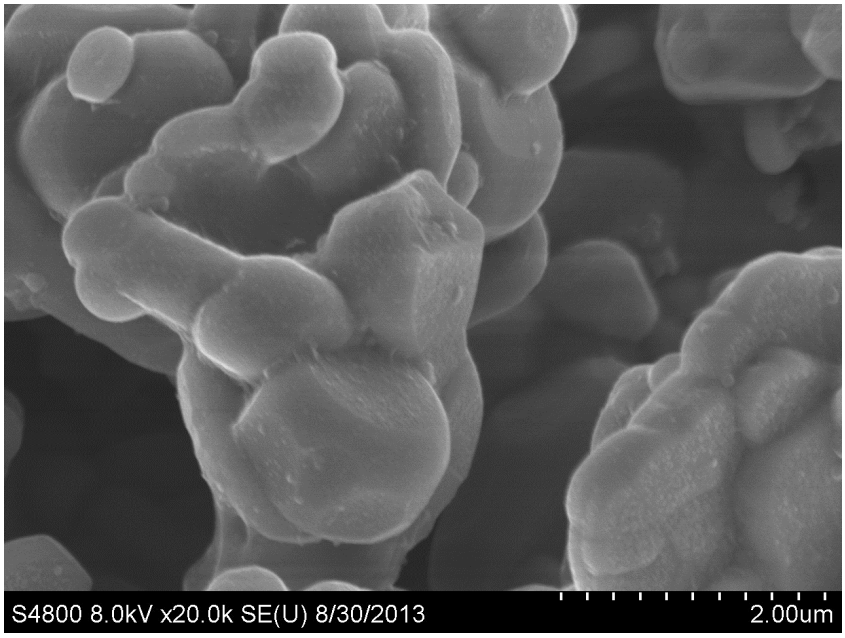
a) Full size SEM image of the raw cathode surface.



b) Full size SEM image of the cathode surface cycled in reference electrolyte between 2.5 - 4.6 V(*vs.* Li/Li^+).



c) Full size SEM image of the cathode surface cycled in electrolyte with 1 mM HDI added between 2.5 - 4.6 V(*vs.* Li/Li^+).



d) Full size SEM image of the cathode surface cycled in electrolyte with 100 mM HDI added between 2.5 - 4.6 V(*vs.* Li/Li^+).