## Construction of a stable interface in the cathode of $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$

## by LiDFOB electrolyte additives for high-performance sodium-ion

## batteries.

Siyao Li, Hui Xu\*, Yuanqiang Zhu, Ziwei Yang, Yuanhai Bao, Yong Chen\*. College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou, 730050, China.

\*Corresponding author. Tel: +86—13639317927

E-mail address: xuhui@lut.edu.cn. yongchen2003@126.com

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Molecule	Structure	E <sub>HOMO</sub> /eV	E <sub>LUMO</sub> /eV
EC	° °	-6.903	-0.295
DEC	~~~~	-7.221	-0.090
PF <sub>6</sub> -	$F \xrightarrow{F} F$ $F \xrightarrow{F} F$	-0.12	0.189
DFOB-		-0.075	0.057

Table S1. The HOMO and LUMO energy levels of EC, DEC, PF<sub>6</sub><sup>-</sup>, DFOB<sup>-</sup>.

No.	EC	DEC	LiDFOB	NaPF <sub>6</sub>
D1	50%	50%	0.2 wt%	1.0 M
D2	50%	50%	0.4 wt%	1.0 M
D3	50%	50%	0.6 wt%	1.0 M
D4	50%	50%	0.8 wt%	1.0 M
D5	50%	50%	1.0 wt%	1.0 M

 Table S2. Contents of each component in the five groups of electrolytes.

Electrolyte		1 <sup>st</sup>	10 <sup>th</sup>	20 <sup>th</sup>	30 <sup>th</sup>	40 <sup>th</sup>
0 wt%	$R_{CEI}/\Omega$	1260	1012	1309	1140	660.1
	$Rct/\Omega$	174.8	555.1	535.5	470.2	763
0.2 wt%	$R_{CEI}/\Omega$	194.6	483.2	567	569.7	653
	$Rct/\Omega$	3015	6238	15467	3887	4529
0.4 wt%	$R_{CEI}/\Omega$	179.4	344.4	394.3	213.9	89.28
	$Rct/\Omega$	8276	8251	9442	2446	2588
0.6 wt%	$R_{CEI}/\Omega$	107.8	195.4	638.2	632.3	812.3
	$Rct/\Omega$	9346	12366	3631	6395	7949
0.8 wt%	$R_{CEI}/\Omega$	7.936	82.38	147.1	124.8	126.2
	$Rct/\Omega$	32100	4830	10809	2911	6019

**Table S3.** Fitting results of the equivalent circuit model



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Fig. S2. The equivalent circuit model for impedance fitting



**Fig. S3.** The GITT profiles of P2-NNMO (a) in baseline electrolyte and (b)electrolyte containing 0.8wt% LiDFOB at the voltage range of 2 - 4.2 V.



Fig. S4. (a) Initial charge / discharge curves at 0.1 C (b) Rate capability. (c) Cycling performance at 1 C of the NNMO//HC full cell.



**Fig. S5.** The XPS spectra of NNMO cathode with 0.8 wt% LiDFOB electrolyte of B 1s spectra in the half cell.