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Supporting Information for

Effect approach to improve the electrochemical performance of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material by MOF-derived coating

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Experimental section

The synthesis of NH_2-MIL-53 (Al) was carried out as reported elsewhere.[1] Briefly, aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, 3.863 g, 16 mmol) 2-aminobenzene-1,4-dicarboxylate (abdc, 2.898 g, 16 mmol) was dissolved in 60 mL deionized water in a 100 mL Teflon-lined autoclave and heated at 150 ˚C for 9 h to form light yellow powder. After cooling to room temperature, the products were separated by centrifugation, then heated in N,N-dimethylformamide (DMF) at 150 ˚C for 24 h to remove the remaining abdc, during which the solvent was decanted and repeatedly replenished. After that, the products were immersed in dichloromethane and sonicated for 2 h, during which the solvent was replenished three times. The solvent was removed under vacuum at 150 ˚C for 12 h, yielding the degassed MOF powders.

$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622) was prepared through a co-precipitation method as following procedure.[2]

First, the $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ precursor was synthesized by co-precipitation method. First, nickel acetate ($Ni(CH_3COO)_2 \cdot 4H_2O$), manganese acetate ($Mn(CH_3COO)_2 \cdot 4H_2O$) and cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$), (mol.% of Ni:Co:Mn = 6:2:2) were dissolved in distilled water with a total concentration of 2 mol L^{-1}, and the solution was slowly dripped into a reactor. 4 mol L^{-1} NaOH and 1 mol L^{-1} NH_4OH solutions were simultaneously fed into the reactor. The solution was kept at 50 °C with the pH carefully controlled by the rate of NaOH addition to 11 under vigorous stirring for 12 h. After the reaction, the precursor $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ was filtered, washed, and dried at 110 °C. Second, $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ was synthesized by mixing stoichiometric of $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ precursor and 5 mol.% excess LiOH to account for evaporation of lithium at high temperature, then the mixture was sintered at 470 °C for 5 h and calcined at 850 °C for 5 h in air at a heating rate of 5 °C min^{-1}.

MDA@NCM622 was synthesized through a simple mechanochemical synthetic procedure. Reactions were carried out in a ball mill (QM-3B, Nanjing University Instrument Factory, China) using an 80 mL PTFE grinding jar with five 10 mm zirconia balls. A solid mixture of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (1 g), NH_2−MIL-53 (50 mg) and ethanol (200 μL) was placed into the jar and ground at high speed for 0.5 h.

The as-prepared NH_2−MIL-53@NCM622 was transferred into a tube furnace and were annealed at 600 °C for 3 h in air under constant heating and cooling rates of 5 ˚C min^{-1}.

Al_2O_3@NCM622 was conducted in a similar strategy through a simple mechanochemical synthetic protocol by treating as-synthesized $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ with Al_2O_3 (25 mg, PDF # 46-1212) powders. The powders were placed into the jar and ground at high speed for 0.5 h. The as-prepared Al_2O_3@NCM622 was transferred to a tube furnace and annealed at 600 ˚C for 3 h in air under constant heating and cooling rates of 5 ˚C min^{-1}.

Characterization

Powder X-ray diffraction (PXRD) technology was used to analyze and study the structure of as-prepared and cycled materials using D8 Advance Bruker powder diffractometer equipped with Cu Kα (λ = 1.54178 Å) radiation at a scan rate of 10˚ 2θ/min. Fourier transform infrared (FT-IR) spectra were carried out using a Bruker ALPHA FT-IR Spectrometer. Morphology of the particles was determined by field emission scanning electron microscopy (FESEM, JSM 7500F, JEOL) and transmission electron microscopy (TEM, JEM-1200EX, JEOL). Elemental mappings were recorded by a JEOL 2100F transmission electron microscope operated at 200 kV. ICP-MS (Inductive coupled plasma mass spectrometry) was tested by Varian 725 inductively coupled plasma mass spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al Kα radiation.

Electrochemical measurements were carried out using coin-type cells (CR2032) assembled in an argon-filled glove box. For preparing the working electrode, a mixture of active material, Super P, and poly (vinyldifluoride) (PVDF) at a weight ratio of 80:10:10 was pasted on a pure aluminum foil. The loading level of active materials is about 2–3 mg cm^{-2}. Lithium foil was used as a counter electrode. A celgard 2400 porous membrane was used as a separator and the electrolyte consisted of a solution of 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1:1, v%). Galvanostatic tests of the assembled cells were performed in the voltage range of 3.0-4.5 V (vs Li^+/Li) at desired current densities at room temperature using a CT2001A Land instrument. EIS data were collected after charging samples at 4.5 V during 30 cycles with amplitude of 5 mV in the frequency range of 1 MHz to 1 mHz by an electrochemical workstation (CHI 760E: CH Instrumental Inc.). Cyclic voltammetry (CV) was performed also using CHI 760E over 3.0-4.5 V at a scanning rate 0.1 mV s^{-1}.

The mass of active material is calculated base on the sum of NCM622 and coating material.

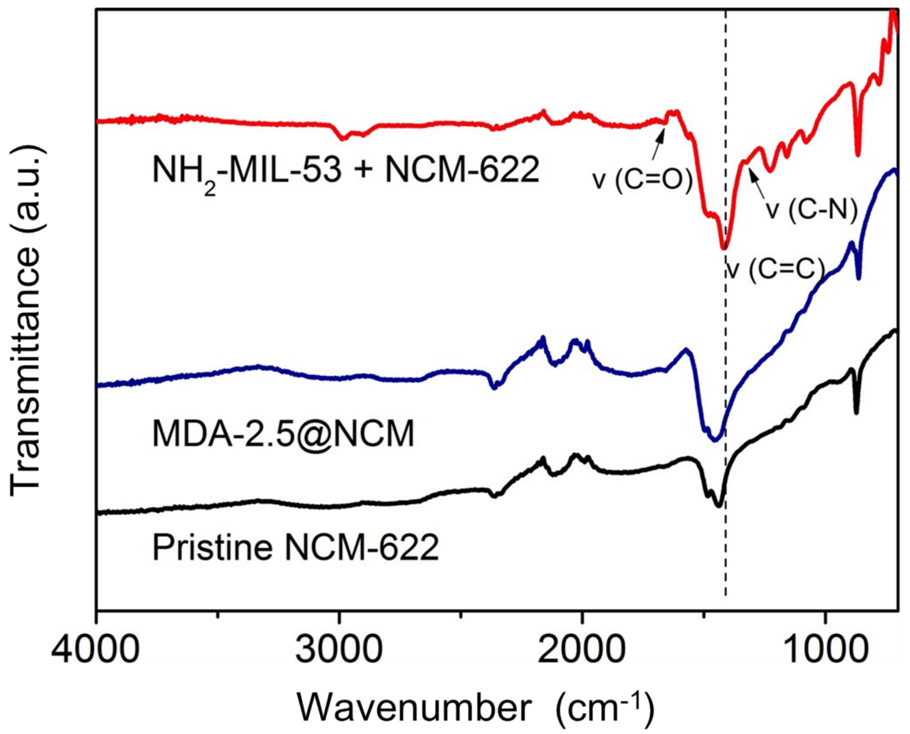

Fig. S1 FTIR images of pristine NCM-622, MDA-2.5@NCM and NH_2-MIL-53 ball milled with NCM-622.

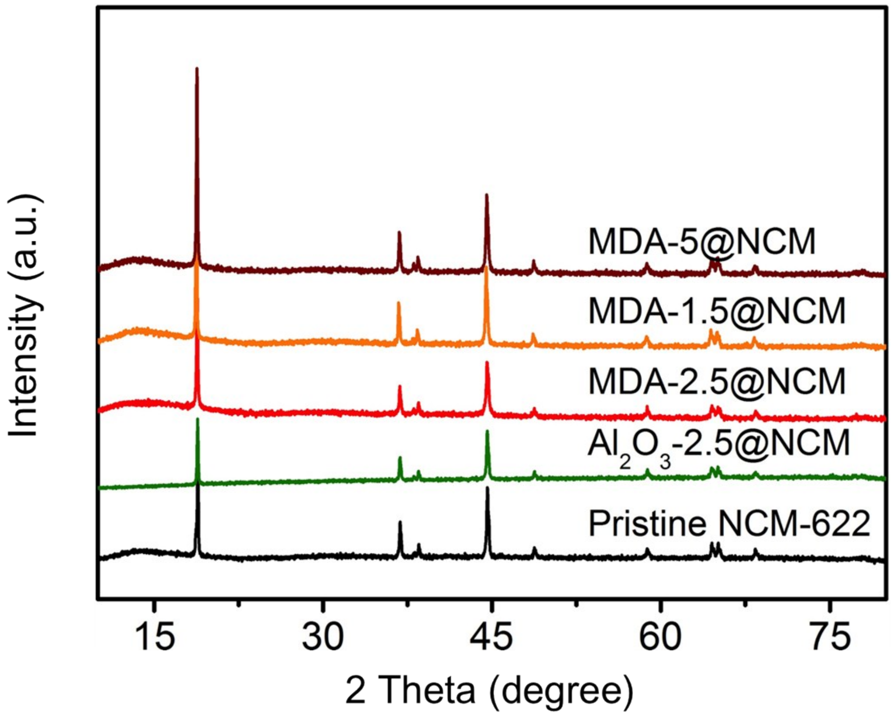

Fig. S2 PXRD patterns of pristine and coated NCM-622.

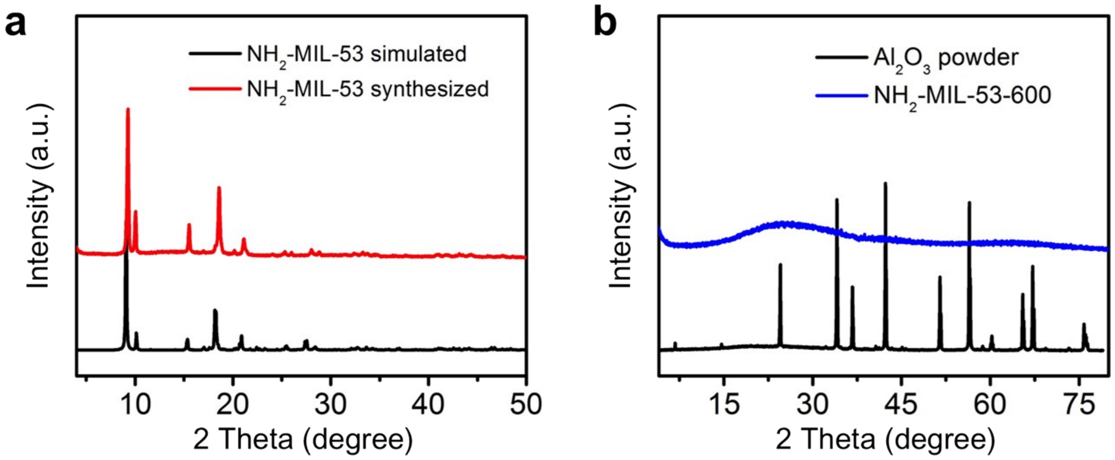

Fig. S3 PXRD patterns of (a) NH$_2$-MIL-53, (b) NH$_2$-MIL-53 after calcination at 600 °C in comparison with pure commercial Al$_2$O$_3$ powder (PDF # 46-1212).

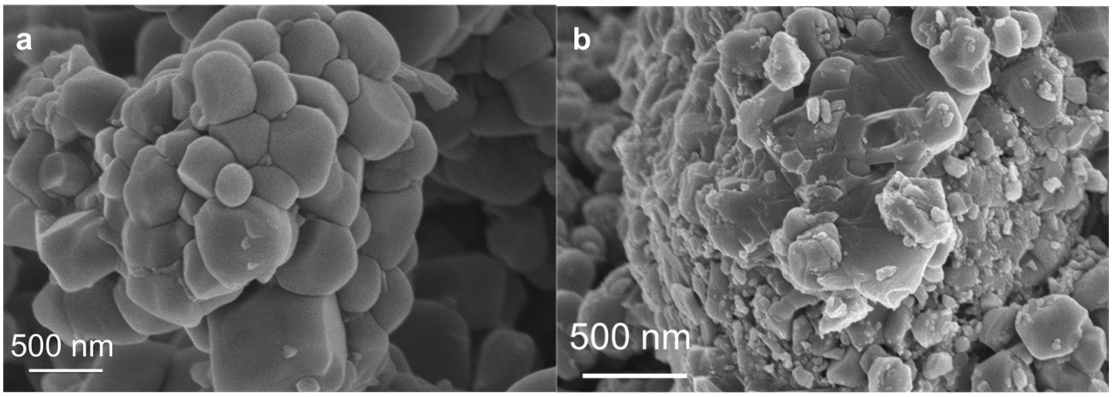

Fig. S4 SEM image of (a) pristine NCM-622 and (b) MDA-2.5@NCM.

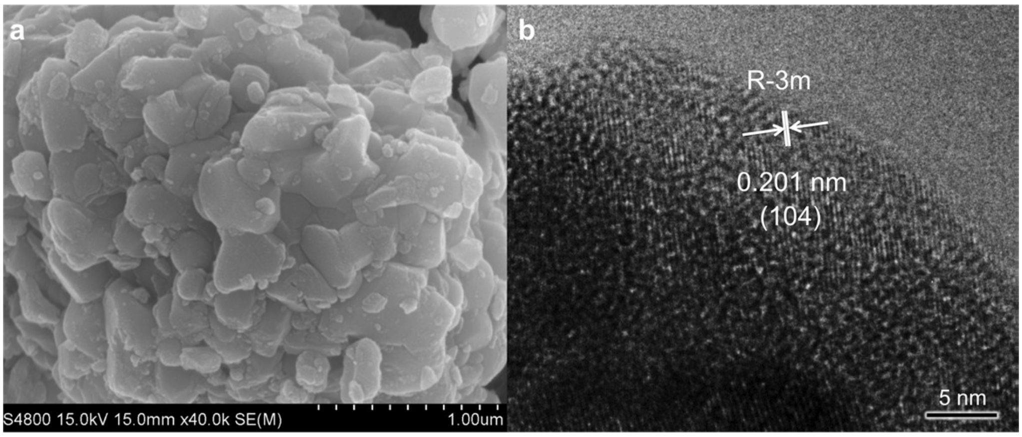

Fig. S5 (a) SEM image and (b) HRTEM image of pristine NCM-622 (ball-milled).

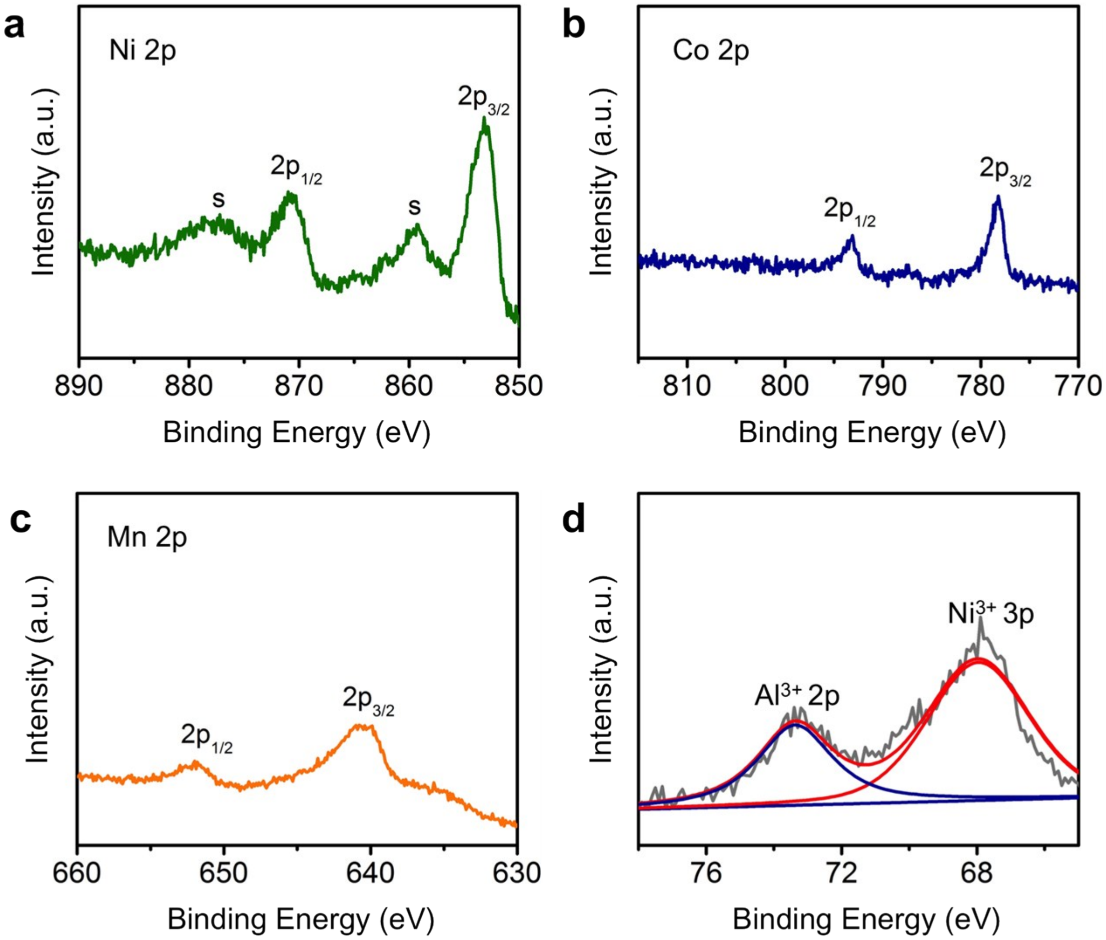

Fig. S6 (a) Ni 2p, (b) Co 2p, (c) Mn 2p and (d) Al 2p XPS data of MDA-2.5@NCM.

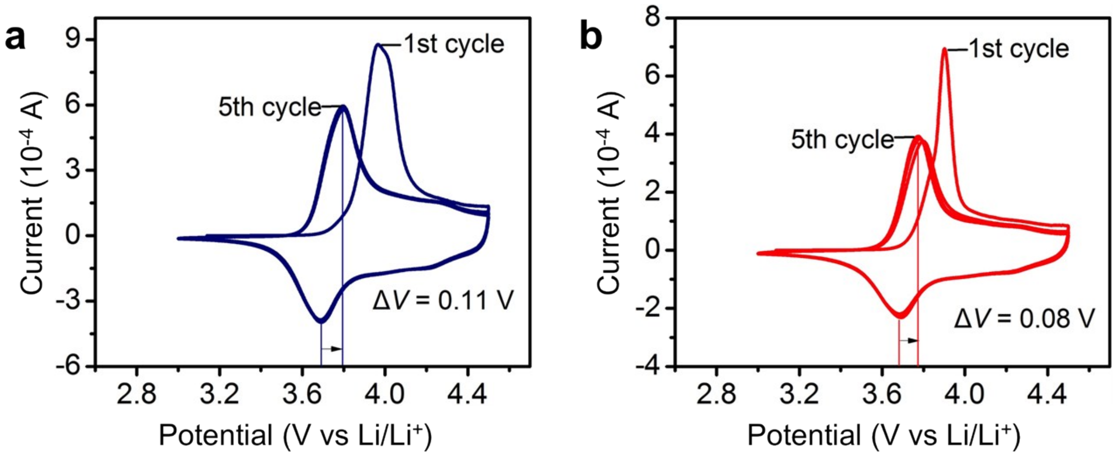

Fig. S7 Cyclic voltammetry of (a) pristine NCM-622 and (b) MDA-2.5@NCM at a scan rate of 0.1 mV s^{-1} over 3-4.5 V for 5 cycles.

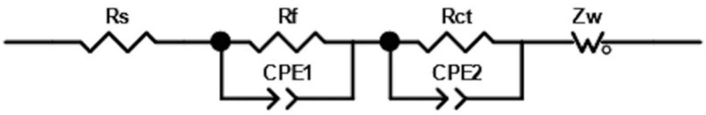

Fig. S8 Equivalent circuit performed to fit the Nyquist plots of in Fig. 4c and 4d.

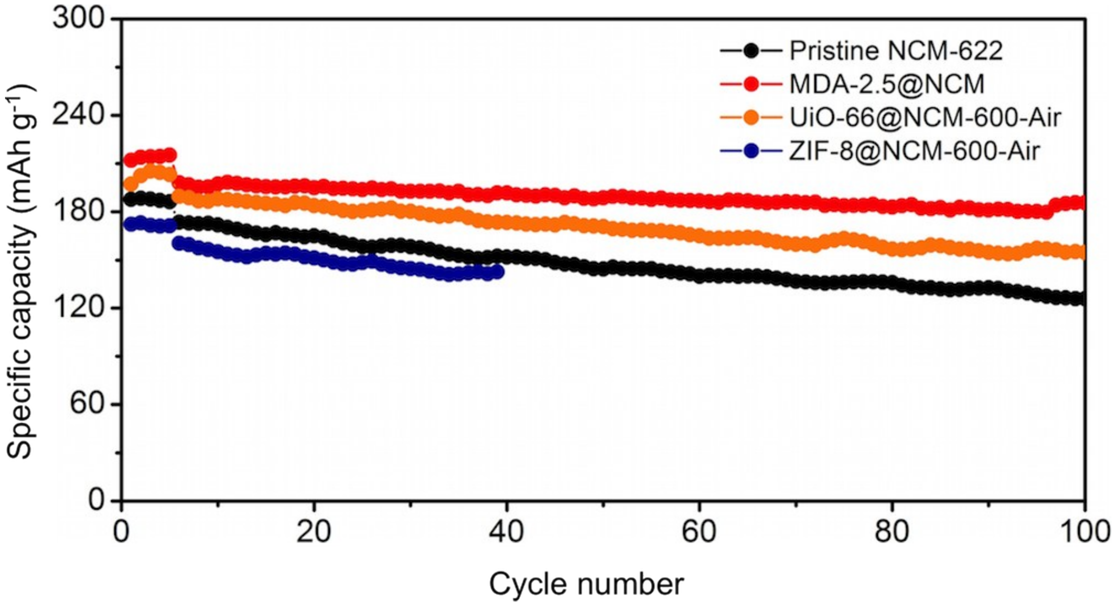

Fig. S9 Cycling performance (0.2 C at first 5 cycles) of the pristine and coated NCM-622 over 3-4.5 V at a current of 1 C (1 C = 140 mA g^{-1}).

Table S1 Impedance parameters fitted for the pristine and coated NCM samples from equivalent circuits of the cells after different cycles.

Samples	Bare			MDA-2.5@NCM		
	R_s	R_f	R_{ct}	R_s	R_f	R_{ct}
1st	4.7	33.9	124.3	3.5	26.2	100.5
100th	11.5	105	1094	5.4	67.3	284.5

Table S2 Different coating materials for NCM-622 (under ambient temperature or 25 °C).

Coating material	Cut off voltage (V)	Current density (mA g^{-1})	1st discharge capacity (mA h g^{-1})	Cycle number	Capacity Retention[a] (%)
MOF-derived alumina (MDA)	3-4.5	28	214.6	-	-
		140	196.5	100	92.7
		280	186.1	100	88.9
		700	168.5	100	78.8
Nano-Al_2O_3[3]	3-4.5	28	197.1	-	-
		140	184.8	30	91.0
		280	~181	-	-
		700	~167	-	-
		1400	~157	-	-
Al_2O_3/conductive polymer[4]	2.6-4.3	36	~173	-	-
		90	170.1	100	96.0
		180	~162	-	-
		900	~136	-	-
TiO_2[5]	3-4.5	28	187.6	-	-
		140	~180	50	88.7
		280	~170	-	-
		700	~142	-	-
SiO_2[6]	3-4.3	0.1 C	175.7	-	-
		0.2 C	~174	-	-
		0.5 C	169.5	50	95.7
		1 C	~161	-	-
		2 C	153.2	-	-

Coating material	Cut off voltage (V)	Current density (mA g^{-1})	1st discharge capacity (mA h g^{-1})	Cycle number	Capacity Retention[a] (%)
PADOT-co-PEG[7]	2.8-4.3	36	~184	-	-
		90	~182	100	93.9
		180	~180	-	-
		900	166.0	-	-
rGO[8]	2.8-4.3	0.1 C	174.2	-	-
		0.5 C	161.2	50	95.7
		1 C	154.9	-	-
		2 C	148.4	-	-
		10 C	105.8	-	-
Li_2ZrO_3[9]	2.6-4.8	27.4	190	50	85
		137	~177	-	-
		274	~166	-	-
Li_3PO_4[10]	3-4.3	28	~172	150	94.1
		280	~168	-	-
		840	~164	-	-
		1400	~160	-	-

[a] Calculated based on the first discharge capacity.

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