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Supplementary Information

Impact of Na_2MoO_4 nanolayers autogenously formed on tunnel-type $Na_{0.44}MnO_2$

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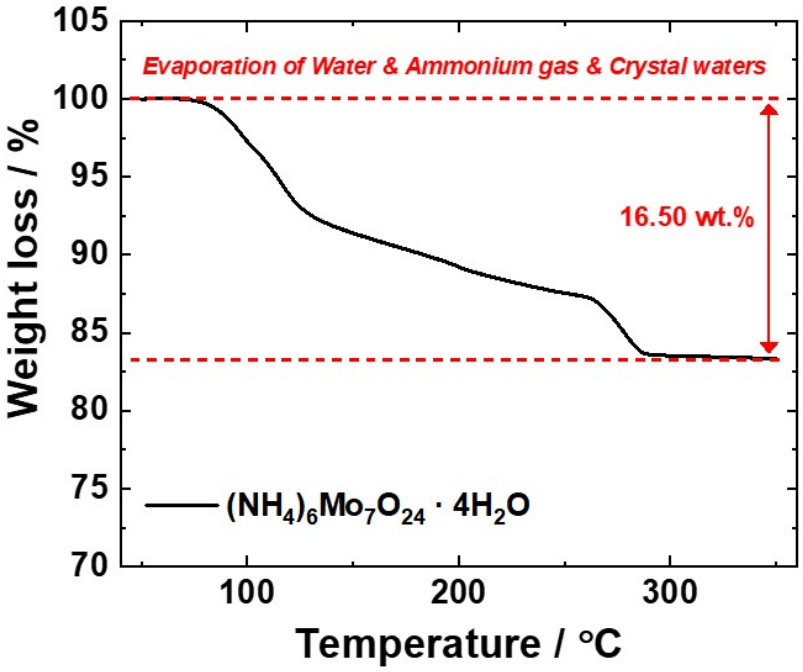

Fig. S1. Thermogravimetric analysis (TGA) curve of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.

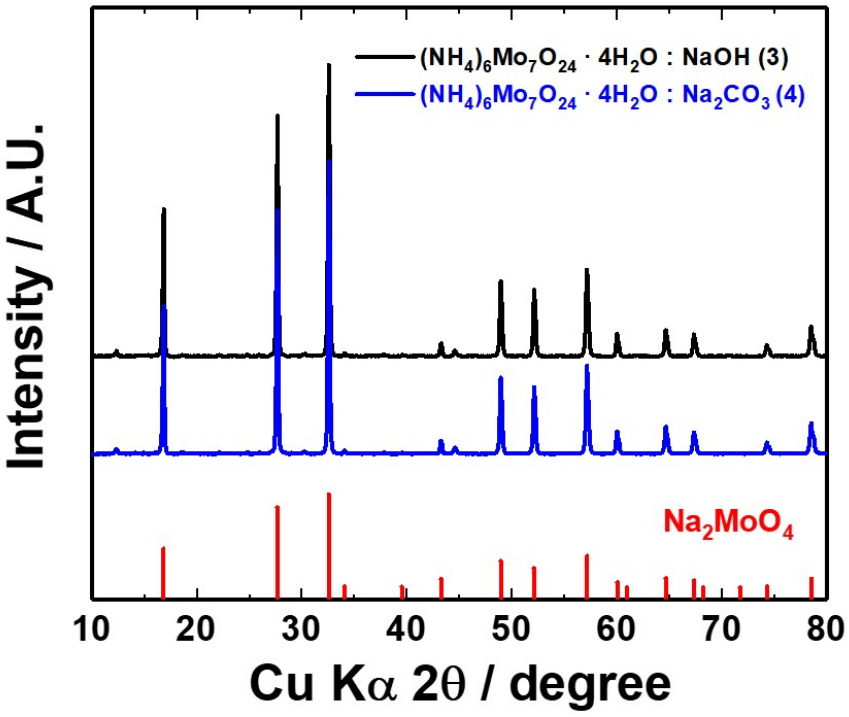

Fig. S2. XRD patterns of Na_2MoO_4 produced in simulated environment obtained at 350 °C for 5 h in air: (top) NaOH + $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and (bottom) Na_2CO_3 + $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$.

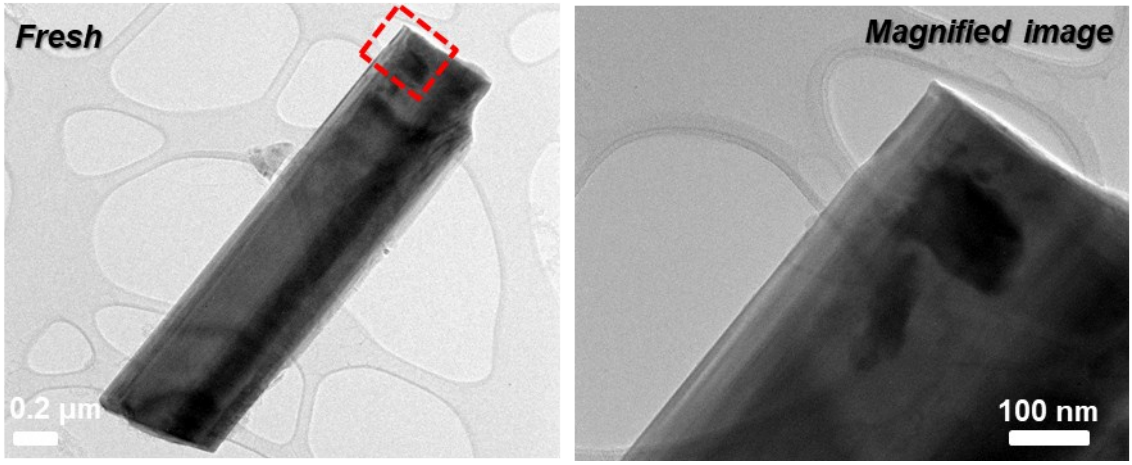

Fig. S3. Bright-field TEM images of the as-synthesized $Na_{0.44}MnO_2$ powders.

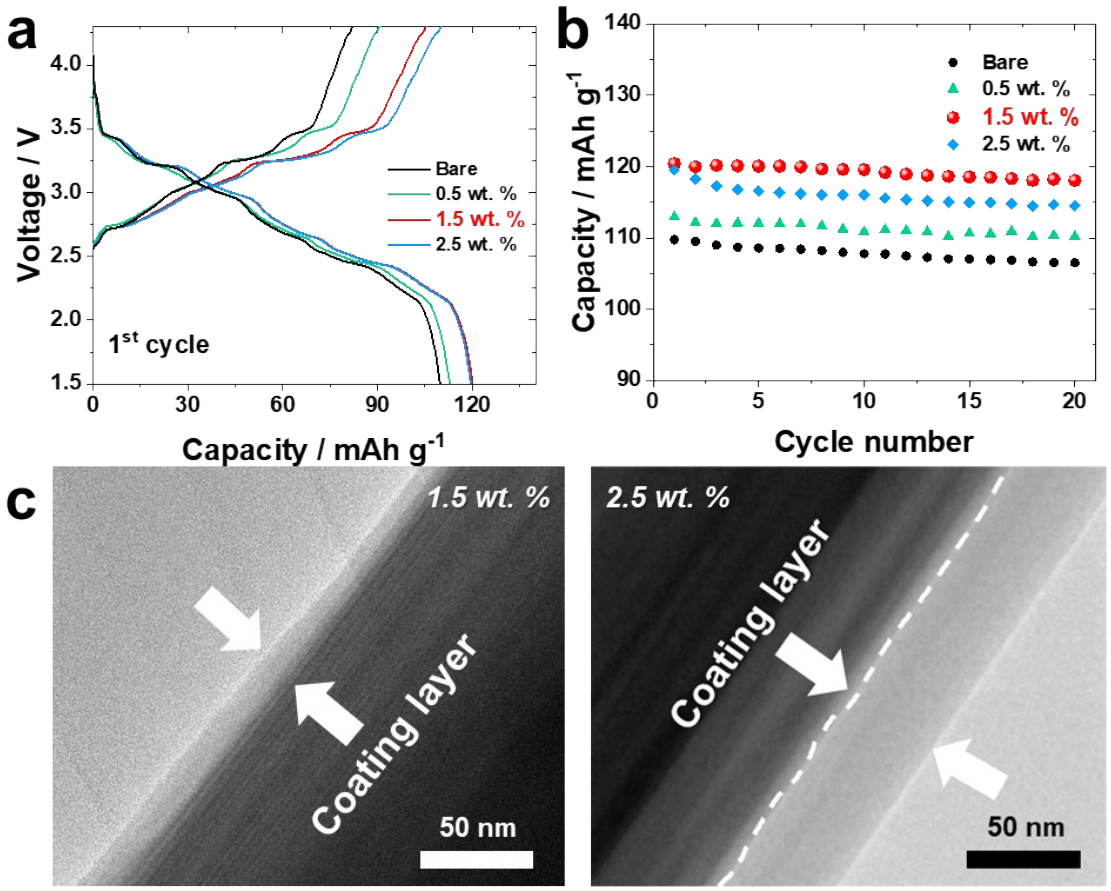

Fig. S4. (a) Charge-discharge curves and (b) cyclability of $Na_{0.44}MnO_2$ with different amount of Na_2MoO_3 coating medium; (c) bright-field TEM images of the 1.5 wt. % and 2.5 wt. % Na_2MoO_3-coated $Na_{0.44}MnO_2$ powders.

Table S1. Rietveld refinement results of XRD data for bare and Na_2MoO_3-coated $Na_{0.44}MnO_2$ compounds.

Formula		**$Na_{0.44}MnO_2$ ($Na_4Mn_9O_{18}$)**		
Crystal system		**Orthorhombic**		
Space group		***Pbam***		
Atom	***x***	***y***	***z***	***g***
Na1	0.2064	0.4155	0.5	0.5
Na2	0.1269	0.0051	0	0.5
Na3	0.2077	0.2051	0	0.5
Mn1	0.3572	0.3061	0.5	0.5
Mn2	0.0142	0.1081	0	0.5
Mn3	0.0314	0.3066	0	0.5
Mn4	0.3618	0.0903	0.5	0.5
Mn5	0	0.5	0	0.25
O1	0.3631	0.0049	0.5	0.5
O2	0.2223	0.0933	0	0.5
O3	0.0496	0.1610	0.5	0.5
O4	0.4181	0.1641	0.5	0.5
O5	0.1621	0.2833	0.5	0.5
O6	0.4100	0.2632	0	0.5
O7	0.3150	0.3562	0	0.2423
O8	0.4999	0.0754	0	0.7084
O9	0.4688	0.4354	0.5	0.7053

Sample	***a*-axis / Å**	***b*-axis / Å**	***c*-axis / Å**	**R_{wp} / %**	**Electrical conductivity / S cm^{-1}**
Bare	9.0976(9)	26.4431(6)	2.8246(9)	8.5%	2×10^{-6}
Coated	9.0920(7)	26.4452(1)	2.8242(2)	8.8%	8×10^{-5}

Table S2. Residual Na_2CO_3 and NaOH contents of bare and Na_2MoO_4-coated $Na_{0.44}MnO_2$ samples from Warder titration.

$Na_{0.44}MnO_2$	pH	Na_2CO_3 [ppm]	NaOH [ppm]	Total [ppm]
Bare	11.37	9,850	7,840	17,690
Coated	11.01	5,616	4,900	10,516

Table S3. HF titration results for extensively cycled bare and Na_2MoO_4-coated $Na_{0.44}MnO_2$ cathode tested in Na cells.

$Na_{0.44}MnO_2$	**HF [ppm]**
Bare	192
Coated	82

Table S4. Comparison of electrode performance for several tunnel-structured cathode materials.

Tunnel-type material	Voltage	Current density	1st discharge capacity	Capacity retention	Rate capability	ref
Bare $Na_{0.44}MnO_2$ *(This work)*	1.5 - 4.3 V	12 mA g^{-1}	110 mAh g^{-1}	72 % over 200 cycles	1 % (7.2 A g^{-1} / 12mA g^{-1})	-
Na_2MoO_4-coated $Na_{0.44}MnO_2$ *(This work)*	1.5 - 4.3 V	12 mA g^{-1}	120 mAh g^{-1}	86 % over 200 cycles	67 % (7.2 A g^{-1} / 12mA g^{-1})	-
$Na_{0.44}MnO_2$	2.0 - 3.8 V	12.1 mA g^{-1}	107 mAh g^{-1}	100 % over 20 cycles	84 % (1.21 A g^{-1} / 12.1 mA g^{-1})	1
$Na_{0.44}MnO_2$	2.0 - 4.0 V	60 mA g^{-1}	108 mAh g^{-1}	97.8 % over 100 cycles	86 % (1.2 A g^{-1} / 12 mA g^{-1})	2
$Na_{0.44}MnO_2$	2.0 - 4.2 V	60 mA g^{-1}	112 mAh g^{-1}	98 % over 100 cycles	73 % (6.0 A g^{-1} / 12 mA g^{-1})	4
$Na_{0.44}MnO_2$	1.5 - 4.0 V	24.2 mA g^{-1}	118 mAh g^{-1}	100 % over 150 cycles	93 % (1.21 A g^{-1} / 24.2 mA g^{-1})	6
$Na_{0.44}[Mn_{0.44}Ti_{0.56}]O_2$	1.5 - 3.9 V	12 mA g^{-1}	110 mAh g^{-1}	90 % over 100 cycles	-	33
$Na_{0.61}Ti_{0.48}Mn_{0.52}O_2$	1.5 – 4.0 V	20 mA g^{-1}	86 mAh g^{-1}	81 % over 100 cycles	36 % (500 mA g^{-1} / 20 mA g^{-1})	44
$Na_{0.61}[Mn_{0.27}Fe_{0.34}Ti_{0.39}]O_2$	2.6 – 4.2 V	8 mA g^{-1}	70 mAh g^{-1}	90 % over 100 cycles	42 % (400 mA g^{-1} / 20 mA g^{-1})	45