Supporting Information

Structure and Performance of $Na_xMn_{0.85}Al_{0.1}Fe_{0.05}O_2$ ($0.7 \leq x \leq 1.0$) Composite Materials for Sodium-ion Batteries

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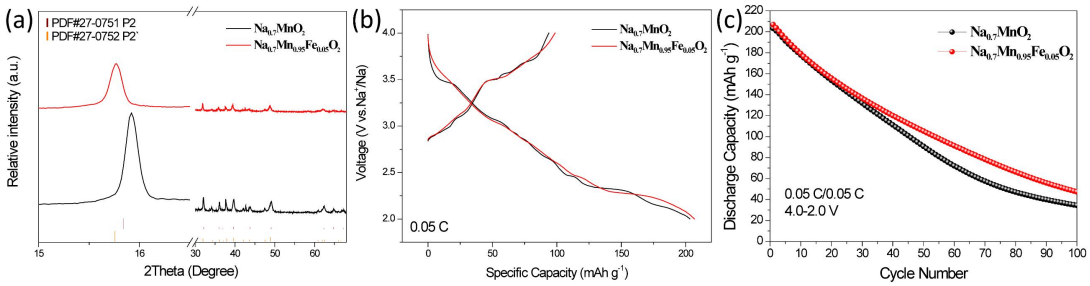

Figure S1. (a) XRD patterns, (b) electrochemical profiles, and (c) cycling performance of $Na_{0.7}MnO_2$ and $Na_{0.7}Mn_{0.95}Fe_{0.05}O_2$ materials.

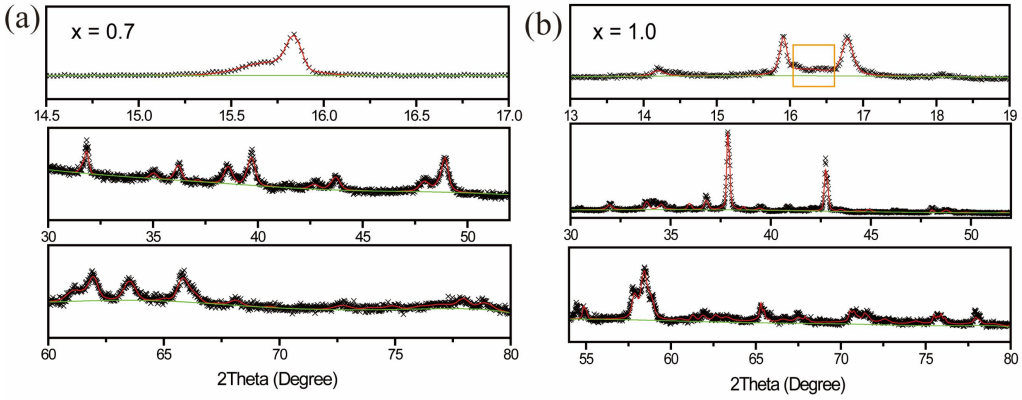

Figure S2. The zoom-in view of Rietveld refinement patterns of (a) $Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$ and (b) $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$.

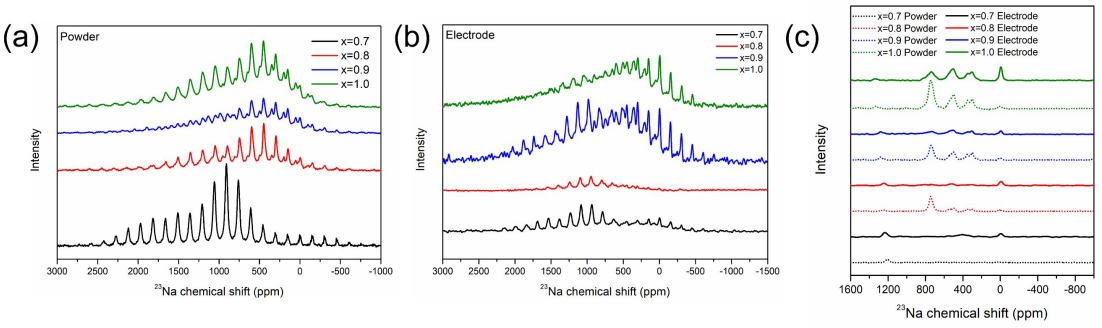

Figure S3. ^{23}Na NMR mapping spectra of (a) the prepared materials and (b) electrodes of $Na_xMn_{0.85}Al_{0.1}Fe_{0.05}O_2$. (c) ^{23}Na pj-MAT PASS NMR spectra of the materials and electrodes of $Na_xMn_{0.85}Al_{0.1}Fe_{0.05}O_2$ ($0.7 \leq x \leq 1.0$).

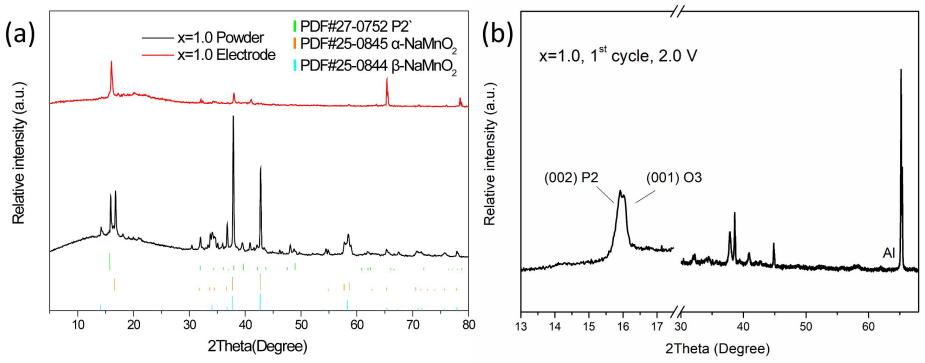

Figure S4. XRD patterns of (a) the powders (tested at 1° min^{-1}), the pristine electrode (tested at 10° min^{-1}), and (b) the electrode after 1 cycle (2.0 V, tested at 5° min^{-1}) of $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$.

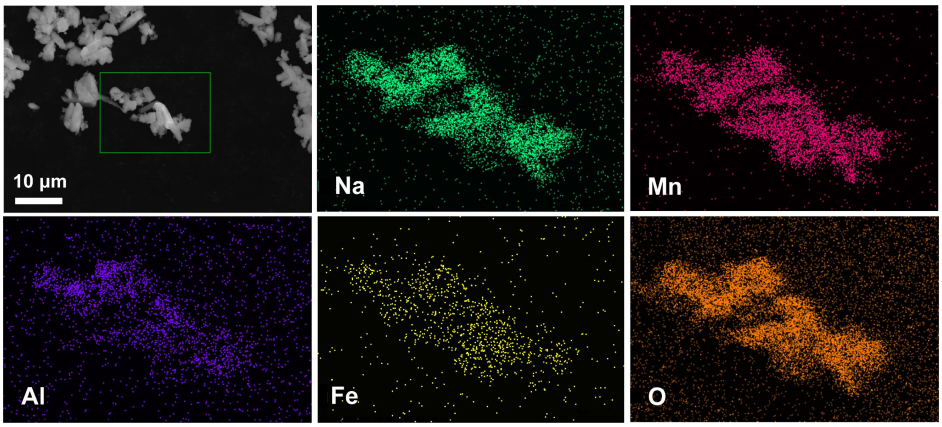

Figure S5. EDS mapping of $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$.

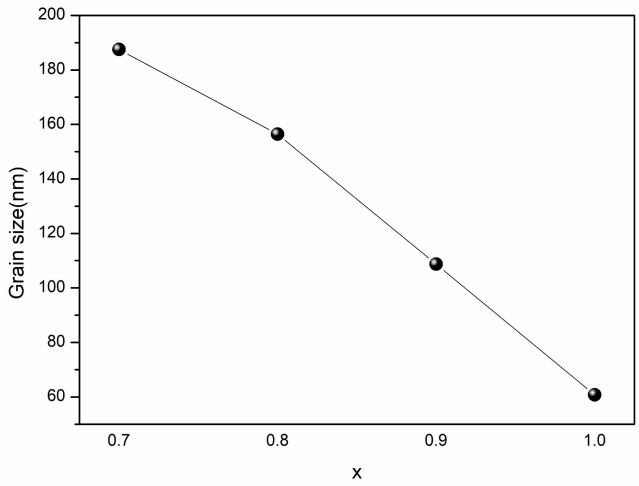

Figure S6. The grain sizes of $Na_xMn_{0.85}Al_{0.1}Fe_{0.05}O_2$ ($0.7 \leq x \leq 1.0$) roughly calculated by Scherrer formula ($L = K\lambda/\beta\cos\theta$).

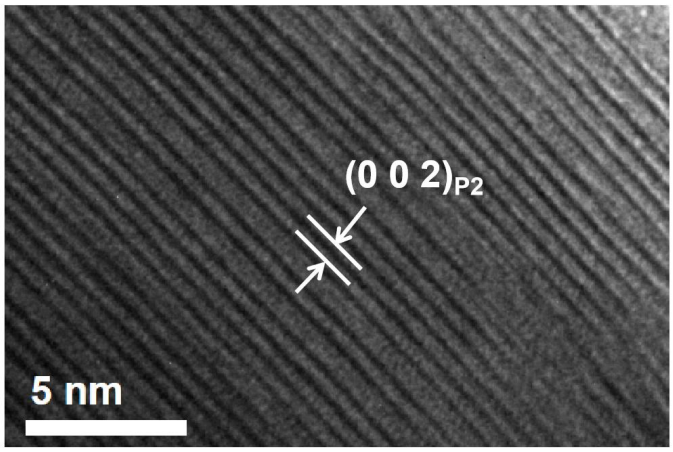

Figure S7. HRTEM image $Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$.

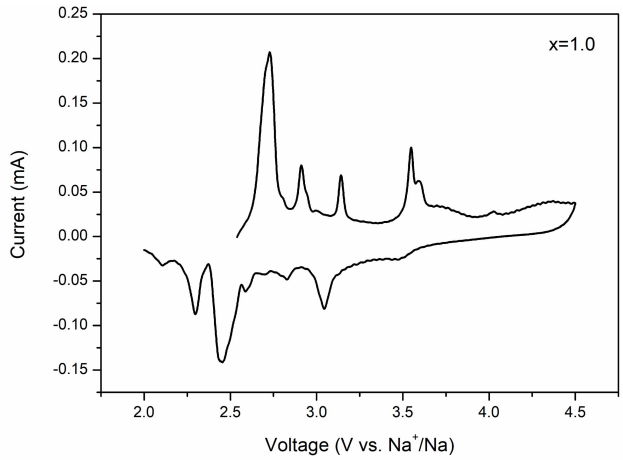

Figure S8. The CV curve of $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$ at a scan rate of 0.03 mV s^{-1}.

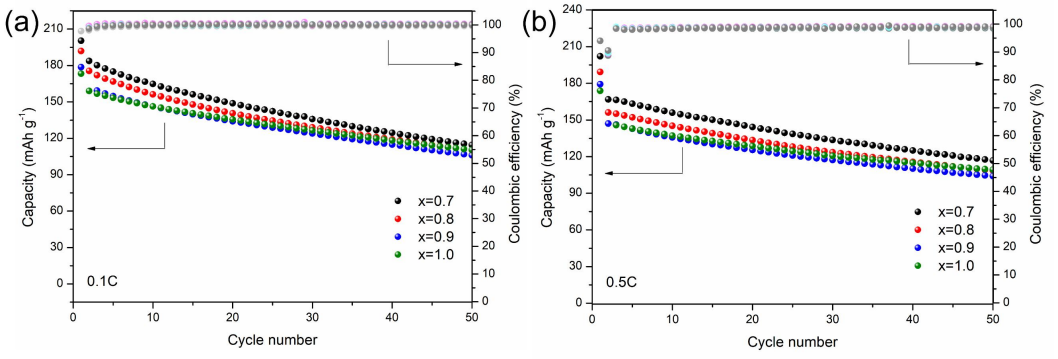

Figure S9. Cycling performance of $Na_xMn_{0.85}Al_{0.1}Fe_{0.05}O_2$ ($0.7 \leq x \leq 1.0$) between 2.0 ~ 4.0 V at (a) 0.1 C and (b) 0.5 C.

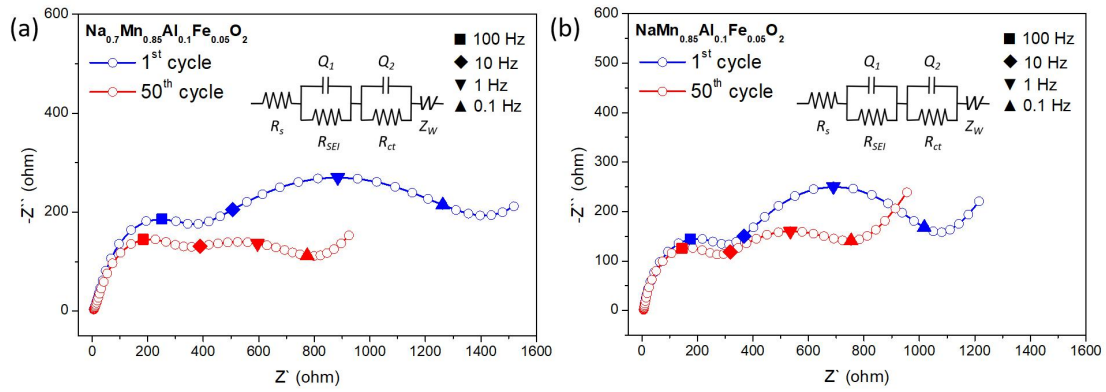

Figure S10. EIS spectra of 1 and 50 cycled (a) Na|$Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$ and (b) Na|$NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$ cells.

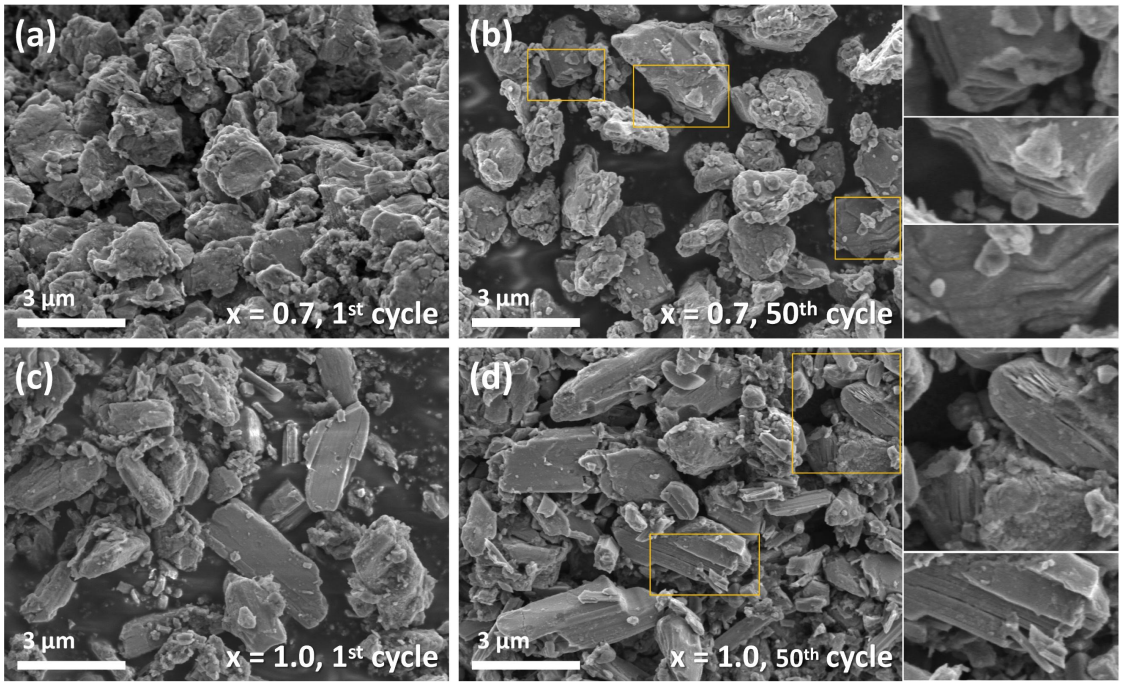

Figure S11. SEM images of $Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$ after (a) 1 cycle and (b) 50 cycles. SEM images of $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$ after (c) 1 cycle and (d) 50 cycles.

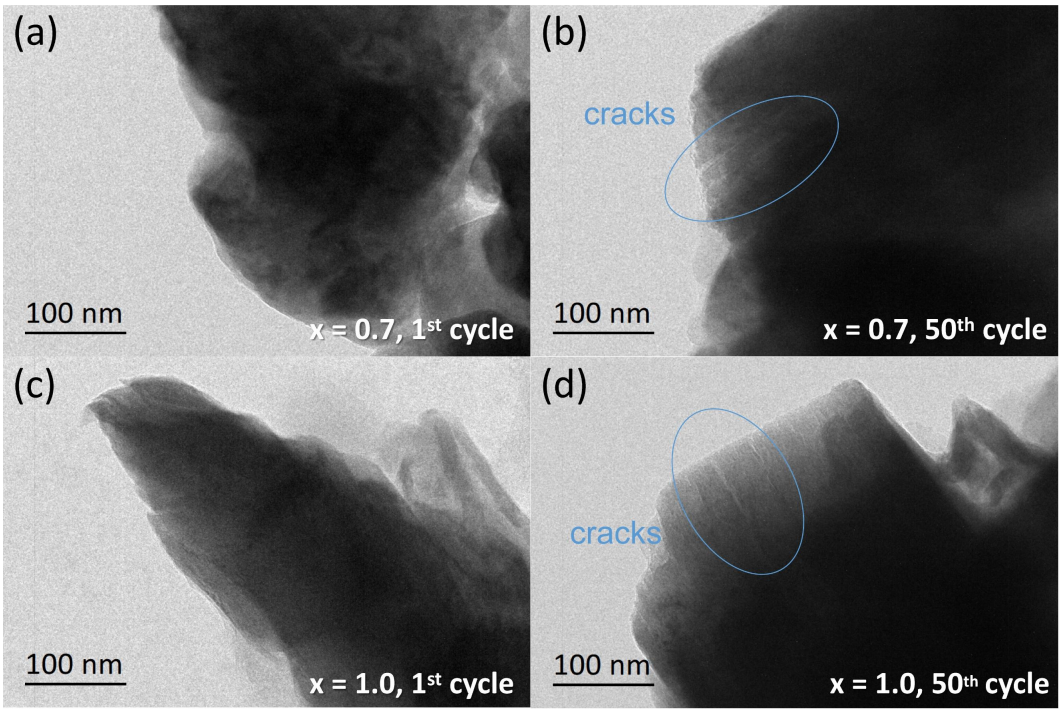

Figure S12. TEM images of $Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$ after (a) 1 cycle and (b) 50 cycles. TEM images of $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$ after (c) 1 cycle and (d) 50 cycles.

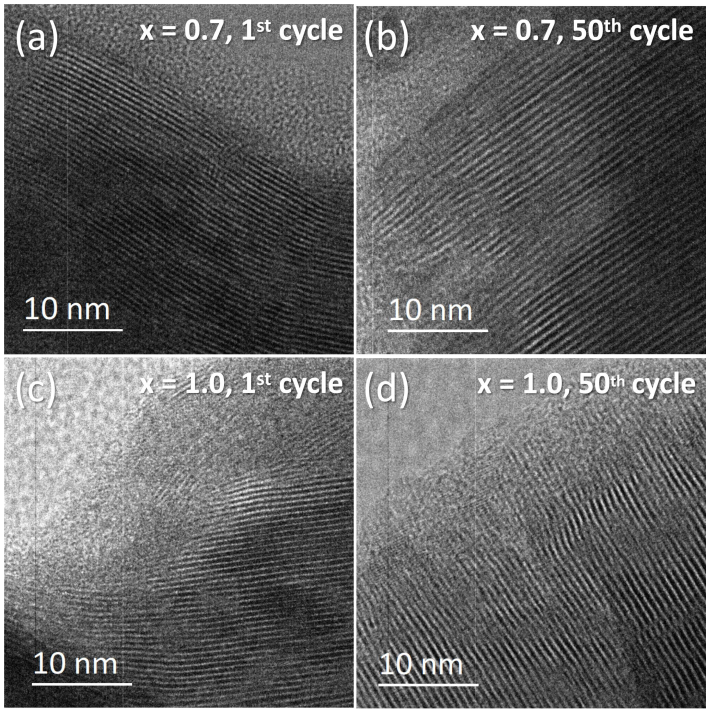

Figure S13. HRTEM images of $Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$ after (a) 1 cycle and (b) 50 cycles. Crystal lattices of $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$. after (c) 1 cycle and (d) 50 cycles.

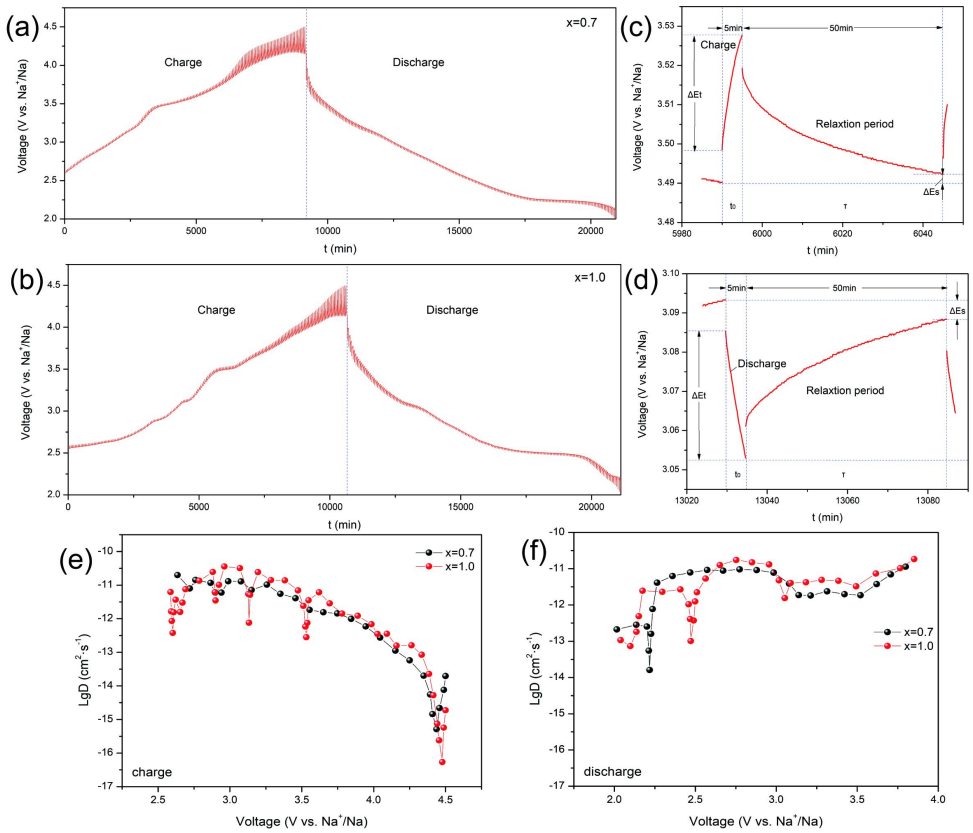

Figure S14. GITT curves of (a) $Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$ and (b) $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$, and the relevant single titration of (c) charge and (d) discharge step GITT curves. The calculated diffusion efficiencies of Na^+ at different voltages of $Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$ and $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$ in (e) charge and (f) discharge process.

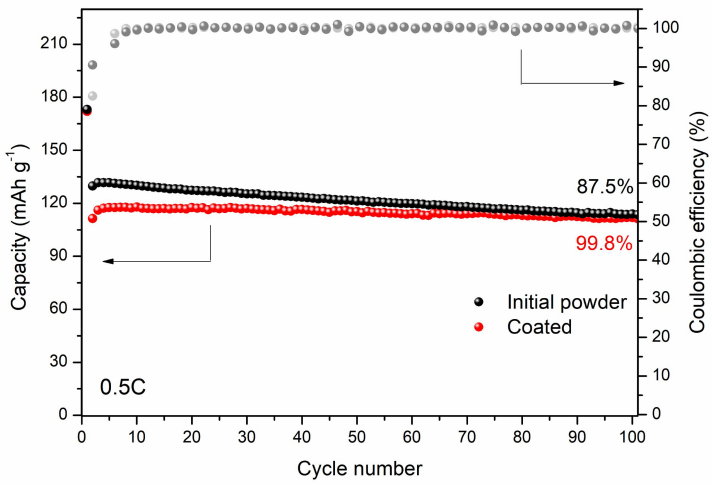

Figure S15. The cycling performance of the analogous composite materials before and after surface coating between 2.0 ~ 4.0 V at 0.5 C.

Table S1. ICP-OES results.

Expected chemical formula	**Measured atomic ratio**			
	Na	Mn	Al	Fe
$Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$	0.641	0.857	0.098	0.045
$Na_{0.8}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$	0.765	0.859	0.096	0.045
$Na_{0.9}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$	0.838	0.859	0.097	0.044
$NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$	0.922	0.852	0.100	0.048

Table S2. Refined lattice parameters of $Na_{0.7}Mn_{0.85}Al_{0.1}Fe_{0.05}O_2$.

Phase		P2'	P2
Space Group		Cmcm	P63/mmc
Cell Parameters	a (Å)	2.845	2.874
	b (Å)	5.141	2.874
	c (Å)	11.317	11.288
	α (°)	90.000	90.000
	β (°)	90.000	90.000
	γ (°)	90.000	120.000
	Volume ($Å^3$)	165.540	80.754
Agreement Factors	Average V_m ($cm^3\ mol^{-1}$)	24.789	
	Rwp (%)	4.86	
	Rp (%)	3.73	
	χ^2	1.07	
	Phase Ratio (%)	79.4	20.6

Table S3. Refined lattice parameters of $NaMn_{0.85}Al_{0.1}Fe_{0.05}O_2$.

Phase		P2'	P2	α-$NaMnO_2$	β-$NaMnO_2$
Space Group		Cmcm	P63/mmc	C2/m	Pmmn
Cell Parameters	a (Å)	2.877	2.736	5.667	4.841
	b (Å)	5.146	2.736	2.863	2.986
	c (Å)	11.256	11.023	5.787	6.419
	α (°)	90.000	90.000	90.000	90.000
	β (°)	90.000	90.000	112.910	90.000
	γ (°)	90.000	120.000	90.000	90.000
	Volume ($Å^3$)	166.635	71.464	86.491	92.793
	Average V_m ($cm^3\ mol^{-1}$)	24.603			
Agreement Factors	Rwp (%)	9.17			
	Rp (%)	6.27			
	χ^2	3.59			
	Phase Ratio (%)	25.0	5.3	41.7	28.0

Table S4. The values of R_{SEI} and R_{ct} after calculation.

	x = 0.7, 1st cycle	x = 0.7, 50th cycle	x = 1.0, 1st cycle	x = 1.0, 50th cycle
R_{SEI} (ohm)	224.4	193.4	279.7	230.0
R_{ct} (ohm)	1231.0	641.0	747.8	555.0