

Electronic Supplementary Information

Design of stable and voidless surface region by intensive subsurface zirconium doping for high performance nickel-rich cathode in sodium-ion batteries

Sunwoo Lee ^a, Donuk Kim ^a and Wonchang Choi^{a*}

^aDepartment of Energy Engineering, Konkuk University, 120, Neungdong-ro, Gwangjin-gu, Seoul 05029, Republic of Korea

*Corresponding author Tel.: +82 2-2049-6051

E-mail address: wchoi@konkuk.ac.kr (Prof. W. Choi)

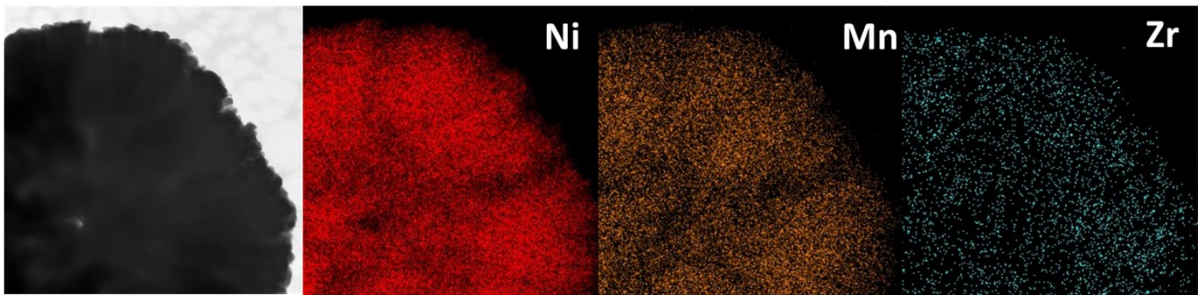


Fig. S1. EDS mapping images of Ni, Mn, and Zr in the Zr5@NM82.

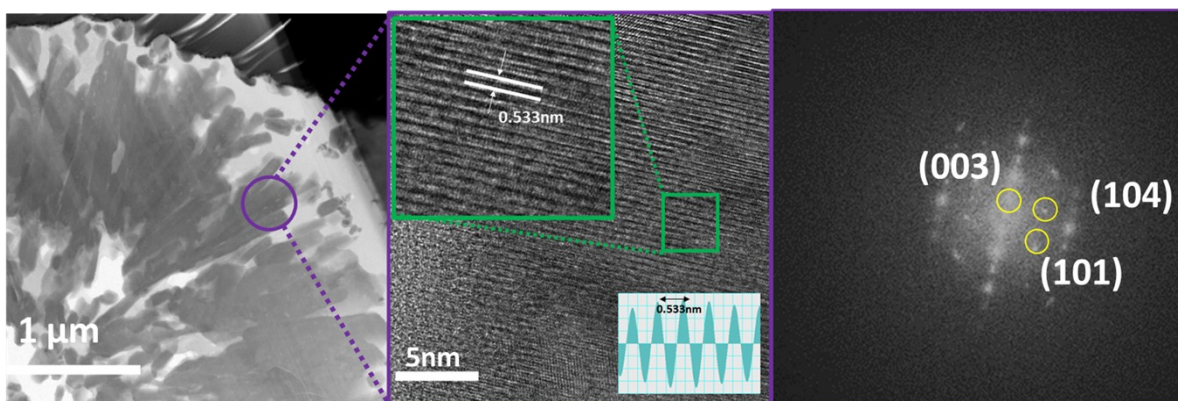


Fig. S2. TEM imagery of the surface of the Pristine.

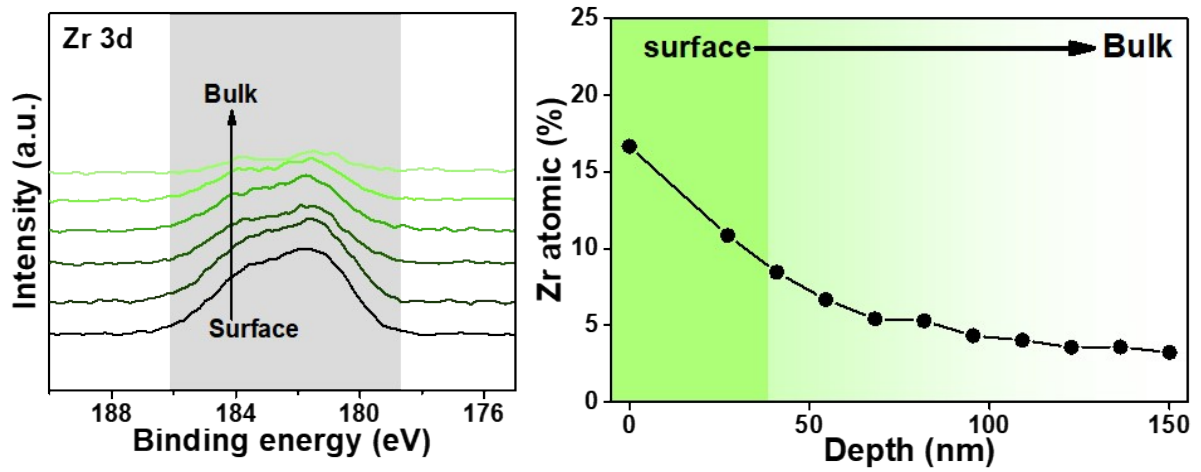


Fig. S3. XPS depth profile of the Zr 3d peak spectra and degree of Zr in Zr5@NM82.

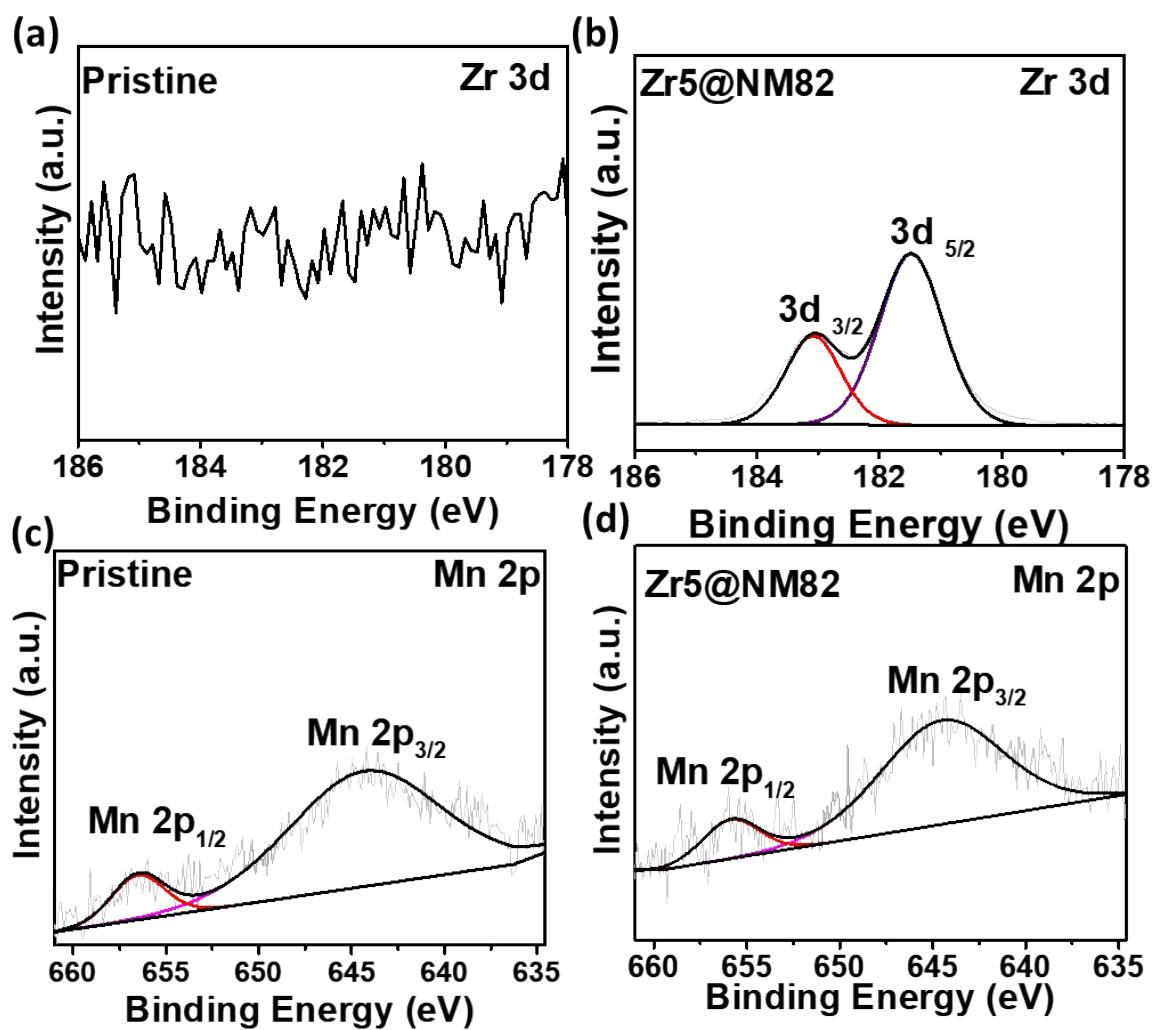


Fig. S4. XPS spectra of the Zr 3d of the (a) the Pristine, and (b) Zr5@NM82, and the Mn 2p of (c) the Pristine, and (d) Zr5@NM82.

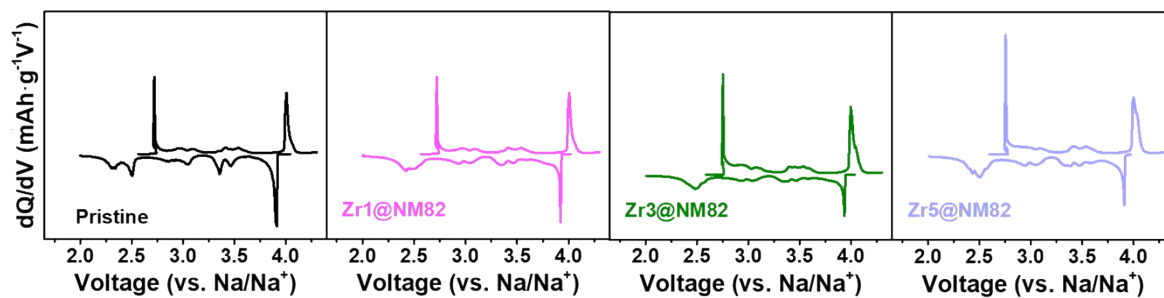


Fig. S5. First cycle dQ/dV plots of the Pristine, Zr1@NM82, Zr3@NM82 and Zr5@NM82 at 0.1 C rate in the range (2.0 – 4.3) V (vs. Na/Na $^{+}$).

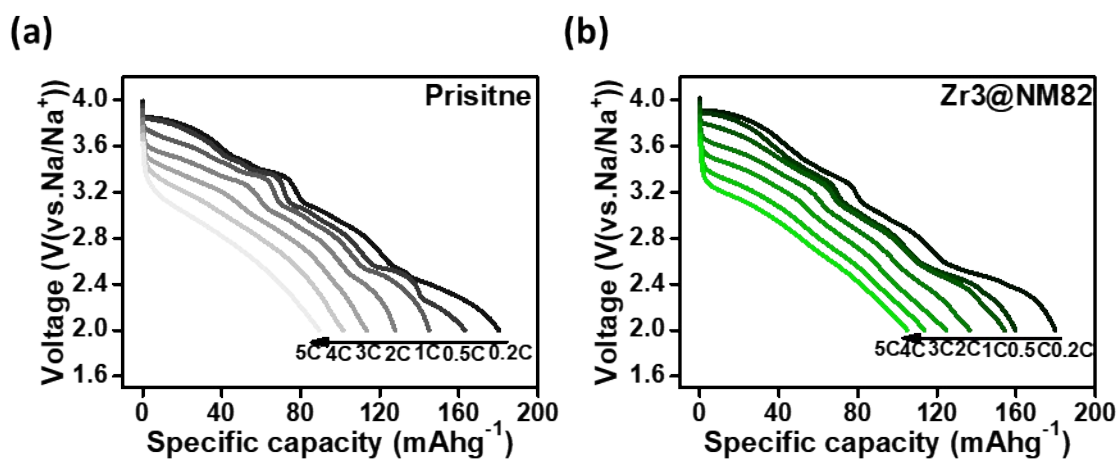


Fig. S6. Discharge voltage profiles of the (a) the Pristine, and (b) Zr3@NM82, in the voltage range (2.0 – 4.3) V (vs. Na/Na⁺) at (0.2, 0.5, 1, 2, 3, 4, and 5) C.

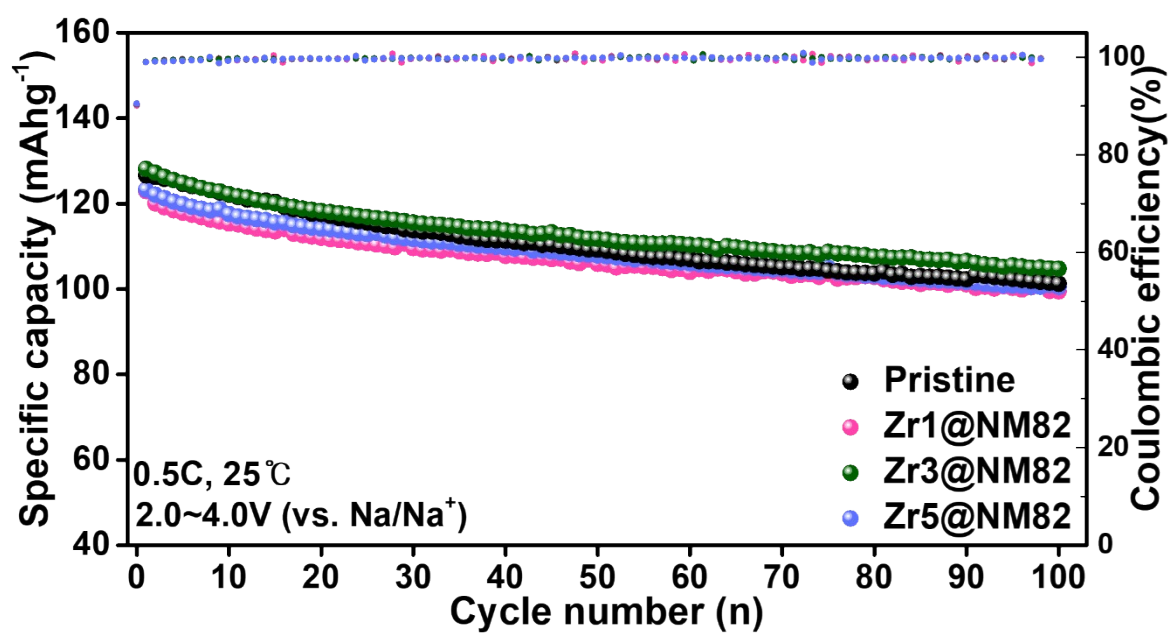


Fig. S7. 0.5 C-rate cycling capability of the Pristine and Zrx@NM82 (x=1,3,5) in the voltage range (2.0 – 4.0) V (vs. Na/Na⁺) at room temperature (25 °C).

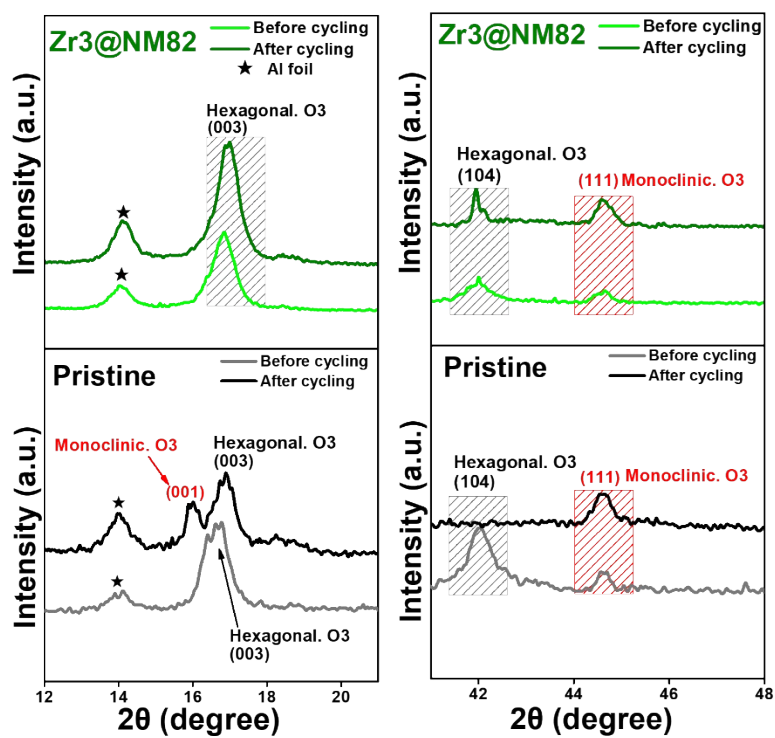


Fig. S8 XRD patterns before and after 100th cycle of Pristine and Zr₃@NM82 at 25 °C

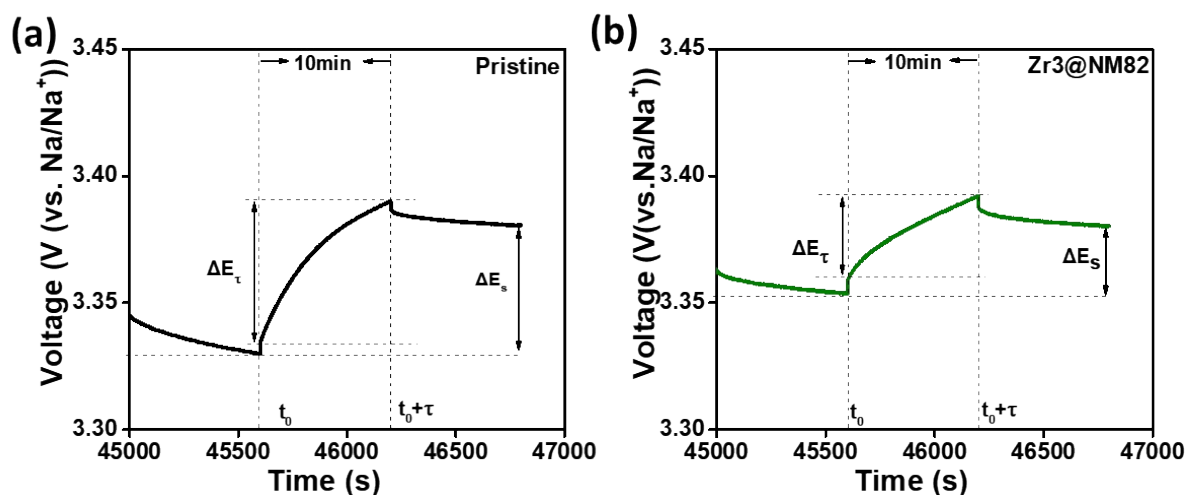


Fig. S9. GITT curves of the (a) the Pristine, and (b) Zr3@NM82, with schematics of a single step during charge at room temperature (25 °C).

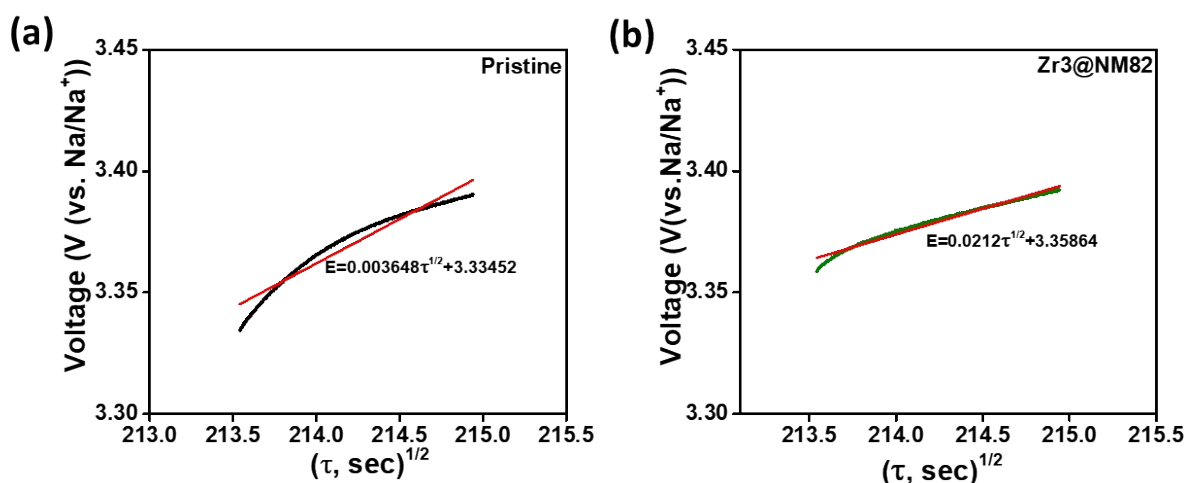


Fig. S10. Linear relationship of E vs. $\tau^{1/2}$ for the (a) the Pristine, and Zr3@NM82.

through GITT analysis. The D_{Na^+} was determined as follows:

After three cycles of charge/discharge at a 0.1 C rate within the (2 – 4.3) V (vs. Na/Na⁺) voltage range, the GITT curve was obtained during the fourth cycle. Charging was conducted at 0.1 C within the (2.0 – 4.0) V range (vs. Na/Na⁺) for 10 min, followed by a 30 min relaxation interval to reach an approximate equilibrium state (E_s). Fig. 6a presents these GITT curves, while Figs. S6a and b show the single-step GITT titration curves (t vs. E profile) for the Pristine and Zr3@NM82 in the (3.325 – 3.4) V range.

The graphs illustrate the process in which the voltage increased due to a current pulse, stabilizing during a 10 min rest period as the internal cell voltage decreased. During the positive current pulse, the potential of the cell increased rapidly in proportion to the IR drop, where R is the sum of the uncompensated resistance (R_{un}) and charge transfer resistance (R_{ct}). Following this, the potential increased slowly to maintain a constant concentration gradient, due to the galvanostatic charge pulse.

At the end of the current pulse during the relaxation time, the current composition inside the electrode became homogeneous, due to Na⁻ion diffusion. Consequently, the cell potential decreased rapidly in proportion to the IR drop, and then slowly reached equilibrium, attaining the open circuit voltage (V_{oc}) of the cell. (The discharge process involves reversing the current, and repeating the relaxation steps).

The chemical diffusion coefficient can be calculated at each step using Eq. (1):

$$D_{Na^+} = \frac{4(m_B V_m)}{\pi(M_B A)} \left(\frac{\Delta E_s}{\tau(dE\tau)/d(\sqrt{\tau})} \right)^2 \quad (\tau \ll L^2/D_{Na^+}) \quad (Eq.1)$$

The symbol τ represents the duration of the current pulse(s). The variable m_B indicates the active mass of the electrode (g), while V_m denotes the molar volume of the electrode ($\text{cm}^3 \cdot \text{mol}^{-1}$). M_B signifies the molecular weight of the Pristine and Zr3@NM82 ($\text{g} \cdot \text{mol}^{-1}$), while A stands for the contact area of the electrode with the electrolyte (BET). L refers to the thickness of the electrode (cm). ΔE_s is the steady-state voltage change (V) due to the current pulse in a single step, while $\Delta E\tau$ represents the voltage change after removing the iR drop during the constant current pulse in a single step.

If E vs. $\tau_{1/2}$ shows linear behavior during the GITT titration, Eq. (1) can be simplified as follows:

$$D_{Na^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2 (\tau \ll L^2 / D_{Na^+}) \quad (Eq. 2) \quad (2)$$

The graphs of E vs. $\tau_{1/2}$ for the pristine and Zr3@NM82 samples in Figs. S7a and b match a straight line. Therefore, Eq. (2) can be used to determine the sodium ion diffusion coefficient (D_{Na^+}) during the charge and discharge processes.

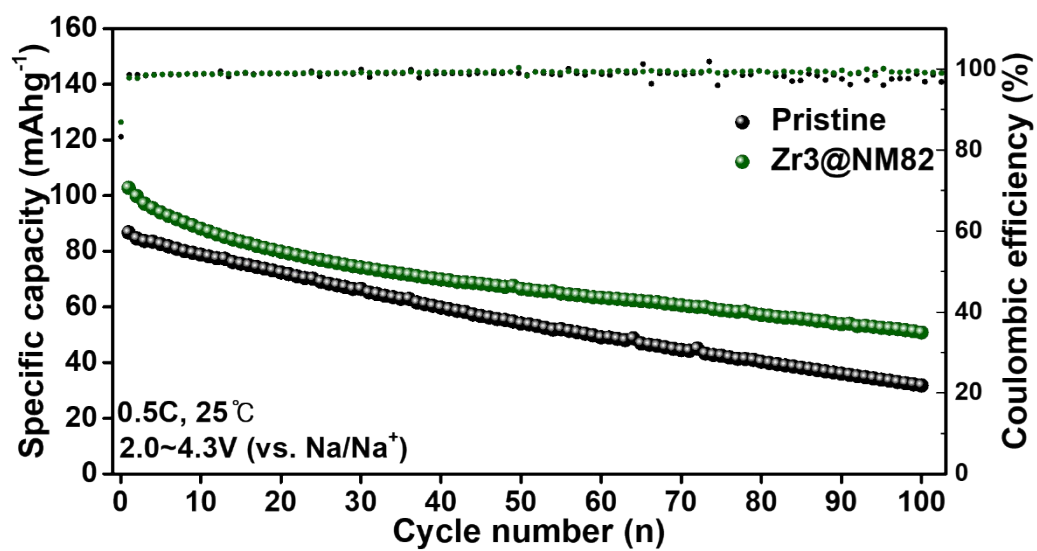


Fig. S11. 0.5 C-rate cycling capability at 25 °C of the Pristine and Zr3@NM82 in the voltage range (2.0 – 4.3) V (vs. Na/Na⁺) after Air stability test.

Table S1. XRD Rietveld refinement data. Lattice parameters, volume, layer distance, crystallite size and c/a ratio of the Pristine, Zr1@NM82, Zr3@NM82, and Zr5@NM82.

Samples	Rietveld Refinement								
	a, b [Å]	c [Å]	c/a ratio	volume (Å ³)	R _p (%)	R _{wp} (%)	TM layer (Å)	Na layer (Å)	Crystallite size (nm)
The Pristine	2.9548	15.7720	5.337	119.34 9	3.33	4.45	2.016	3.250	20.47
Zr1@NM82	2.9554	15.7842	5.342	119.58 3	5.02	6.70	1.964	3.302	24.19
Zr3@NM82	2.9569	15.8093	5.347	119.62 8	3.27	4.51	1.938	3.330	24.40
Zr5@NM82	2.9581	15.8127	5.345	119.69 6	4.93	6.74	1.924	3.337	27.85

Table S2. EIS fitting results for the Pristine and Zr3@NM82 before and after the 50th cycle at 60 °C.

	Before cycles			After 50 th cycle		
	R_s (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)
The Pristine	5.76	39.08	15.11	4.12	77.37	792.0
Zr3@NM82	3.169	28.98	20.12	3.23	69.03	652.20

Table S3. EIS fitting results for the Pristine and Zr3@NM82, before and after the Air storage test.

	Before Air storage test			After Air storage test		
	R_s (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)
The Pristine	5.76	39.08	15.11	3.9294	78.11	108.91
Zr3@NM82	3.169	28.98	20.12	3.299	63.50	49.09