Supplementary Information (SI) for EES Batteries.


# Supplementary Information

## Operando quantification of diffusion-induced stresses in O3-type $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ sodium-ion battery electrode during electrochemical cycling

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### S1. Electrode porosity calculation

The electrode porosity is estimated as follows:

$$Electrode\ Porosity\ (\%) = 1 - \left(\frac{Apparent\ coating\ density}{Theoretical\ compact\ coating\ density}\right)$$

The *theoretical* compact coating density is calculated based on the rule of mixtures, considering the bulk density ($\rho$) and weight fraction of each composite component, as follows:

$$Theoretical\ compact\ coating\ density = \frac{1}{\frac{W_{NFM}}{\rho_{NFM}} + \frac{W_c}{\rho_c} + \frac{W_{binder}}{\rho_{binder}}}$$

where $W_i$ is the weight fraction of the $i^{th}$ component; NFM is $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ and $c$ stands for carbons (Timcal C-45, Tuball SWCNT). The densities of the materials are as reported by the manufacturer and assume no porosity within the particles.

The *apparent* coating density is calculated by the ratio *weight/geometric volume* using several electrode samples from which the average weight and thickness are determined. Naturally, the current collector properties are subtracted in the calculation. The electrode thickness is measured using a digital micrometer.

**Table S1.** NFM111 electrode composition and cell chemistry.

**<u>NFM111 electrode (single-sided; calendered</u>)**

95 wt% $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ (Gelon)

2.95 wt% Timcal C-45 + 0.05 wt.% Tuball SWCNT

2 wt% Solvay 5130 PVDF Binder

| | |
|---|---|
| **Al Foil Thickness** | 20 µm |
| **Total Electrode Thickness** | 156 µm |
| **Coating Thickness** | 136 µm |
| **Porosity** | 34.4 % |
| **Total Coating Density** | 2.75 g/cm$^3$ |
| **Total Coating Loading** | 37.4 mg/cm$^2$ |
| **NFM111 Loading** | 35.5 mg/cm$^2$ |

**Separator**: Glass Fiber (Whatman, Grade GF/F)

**Electrolyte**: 1M $NaClO_4$ in PC + 5 wt% FEC

**Na-metal**: Purchased as cubes (Sigma-Aldrich)

## <u>Figures</u>

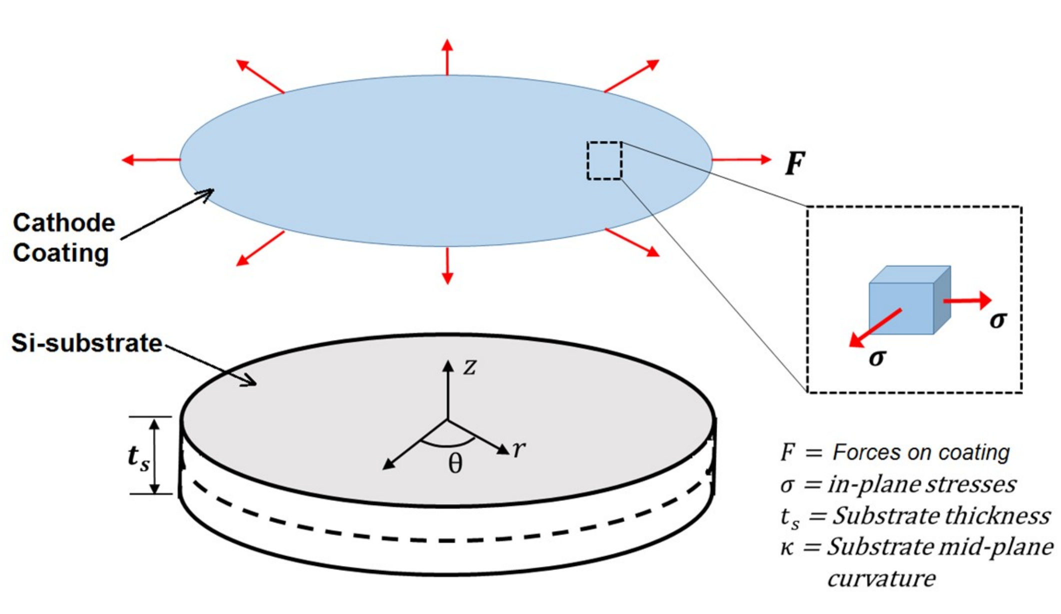


**Fig. S1.** Schematic shows that the typical stress state in a thin film coating on a substrate is in-plane equibiaxial stress (σ), because the expansion/contraction of the film is constrained by the substrate. The out of plane stress, i.e., stress in z direction is zero as the film is free to expand/contract in that direction.[1]

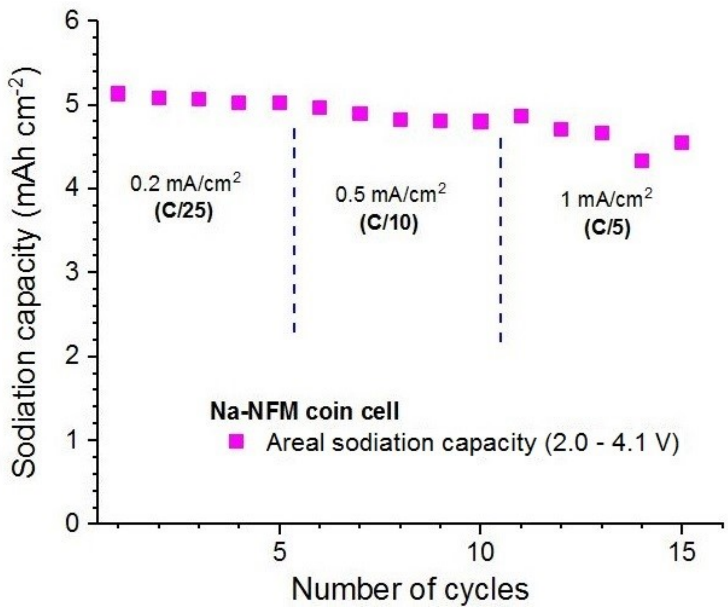



**Figure S2.** Discharge (sodiation) capacity of NFM111 electrode vs. cycle number at the indicated currents. In addition to the NFM111, the coin cell contained a Na-metal counter electrode, glass fiber separator and an electrolyte with 1M $NaClO_4$ salt in PC+ 5 wt% FEC solvent.

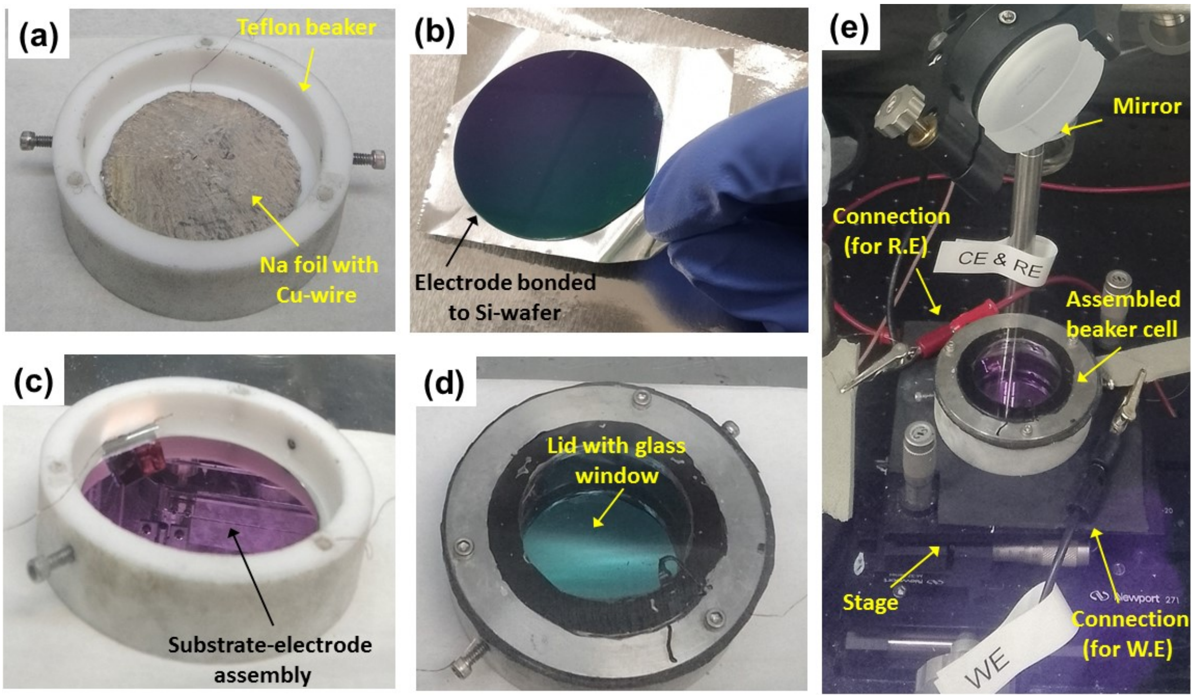



**Figure S3.** Steps of the beaker cell assembly: (a) Na foil with embedded Cu-wire placed in a Teflon beaker, (b) Aluminum current collector of the NFM111 electrode bonded to Si-wafer, (c) NFM111 electrode stacked on top of Na foil with a separator in between to prevent physical contact, (d) covering the beaker with a stainless-steel lid comprising a glass window. (e) shows an assembled beaker cell, placed inside a glovebox, with electrical connections for the electrochemical cycling and optical arrangements for the substrate-curvature measurement.

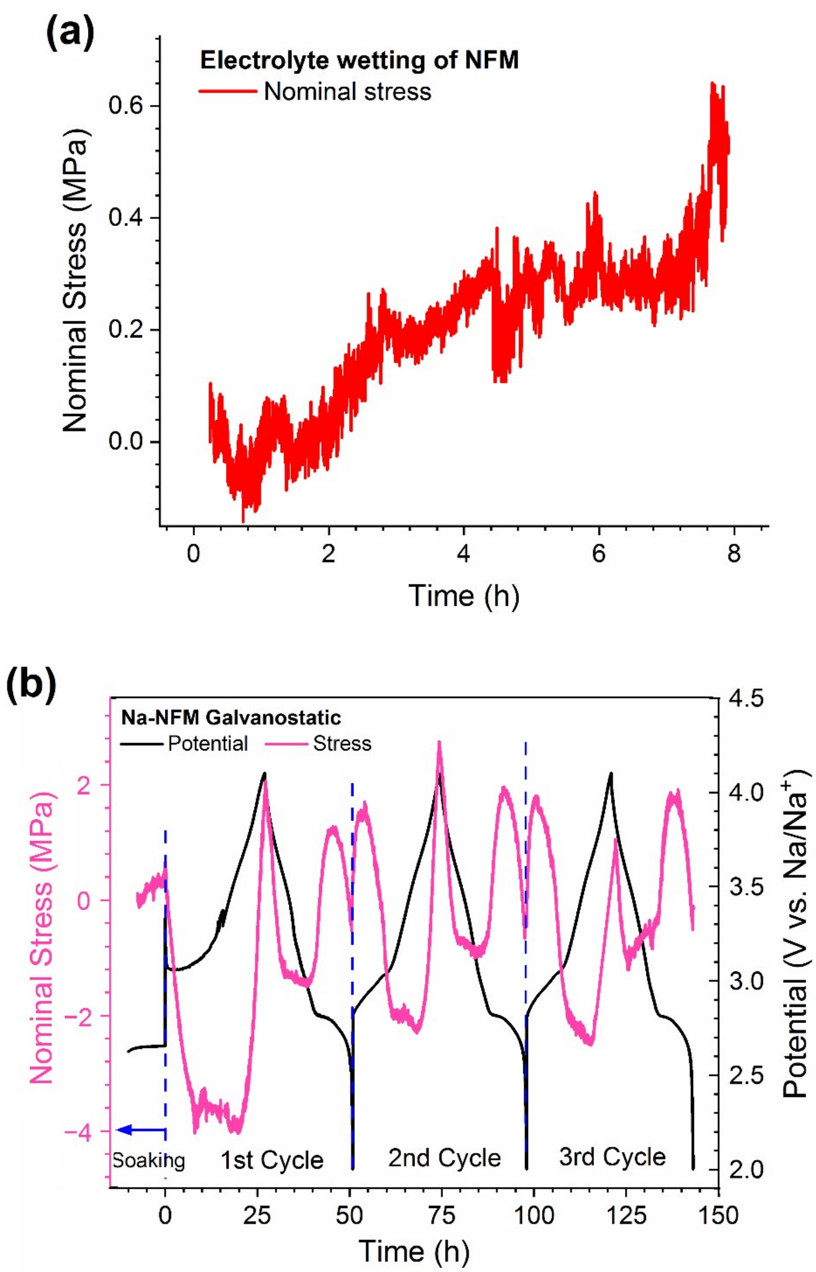



**Figure S4.** (a) Stress evolution in the NFM111 electrode due to wetting by the electrolyte, prior to any electrochemical cycling, (b) Potential and stress evolution in the NFM111 electrode during 3 galvanostatic cycles conducted in a beaker cell, with a current of 0.2 $mA/cm^2$.

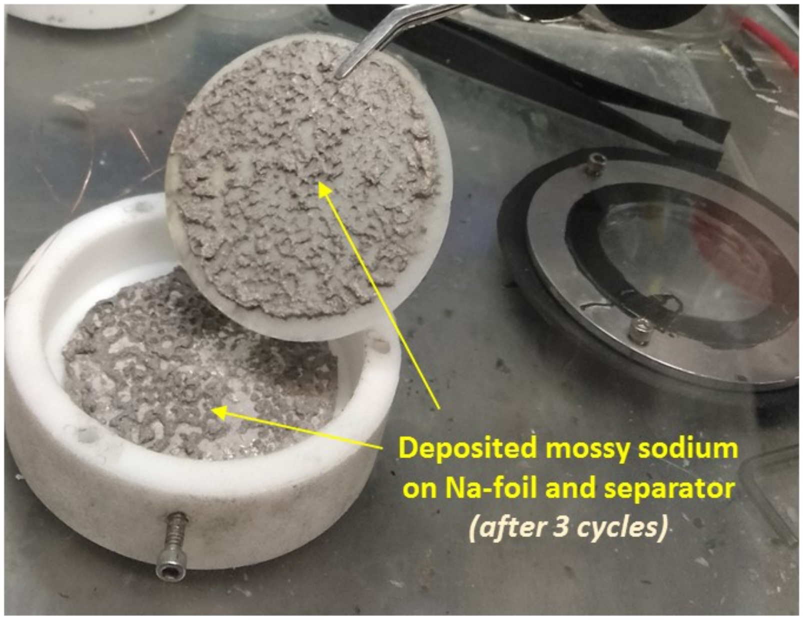



**Figure S5.** Changes to the Na-foil counter electrode after 3 cycles between 2.0 – 4.1 V vs. Na. Note that the high capacity high (~5 mAh cm$^{-2}$) transferred during these cycles aggravates degradation of the Na-metal.

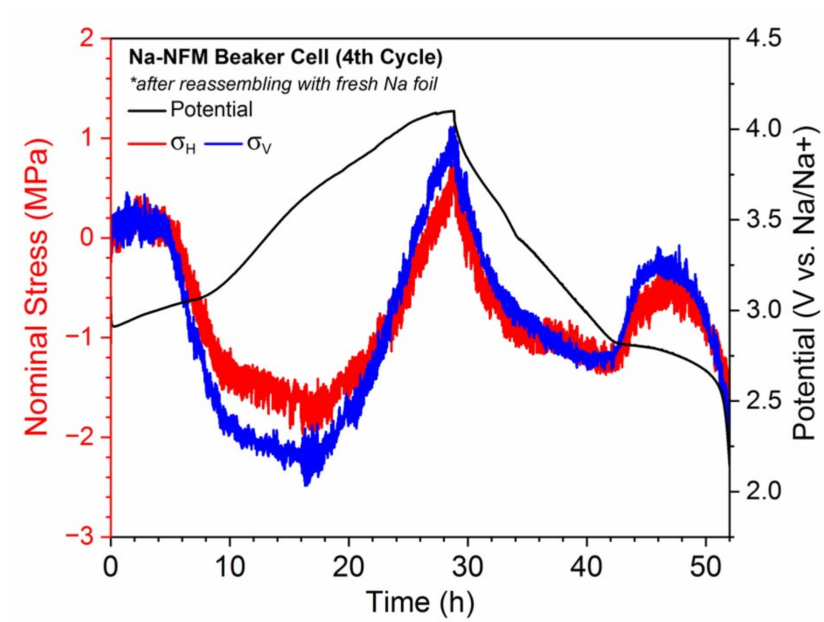
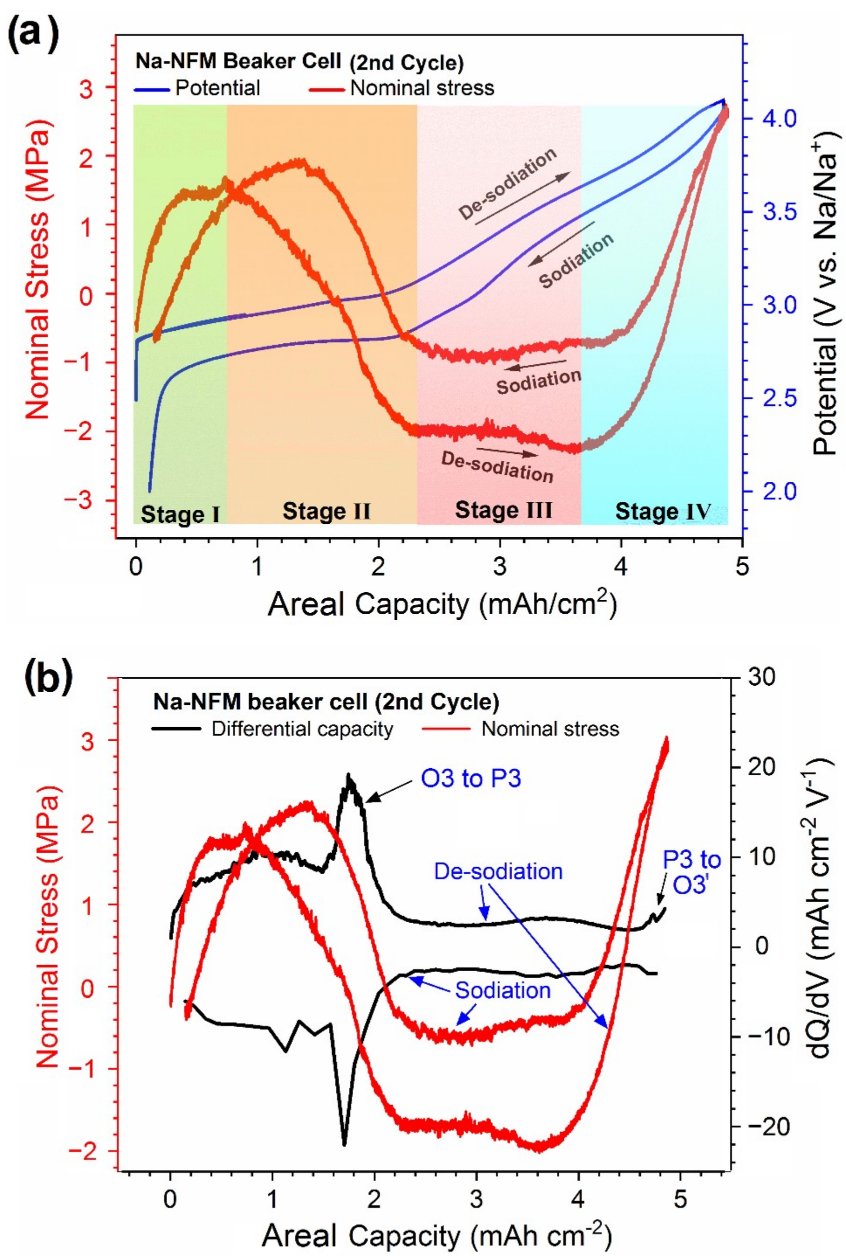



**Figure S6.** Potential and stress evolution in the NFM111 electrode during 4th galvanostatic cycle (after reassembling the cell with fresh Na foil), with a current of 0.2 mA/cm$^2$.



(a)
Na-NFM Beaker Cell (2nd Cycle)
Potential
Nominal stress
De-sodiation
Sodiation
Sodiation
De-sodiation
Stage I
Stage II
Stage III
Stage IV
Nominal Stress (MPa)
Potential (V vs. Na/Na+)
Areal Capacity (mAh/cm2)
(b)
Na-NFM beaker cell (2nd Cycle)
Differential capacity
Nominal stress
O3 to P3
De-sodiation
P3 to O3'
Sodiation
Nominal Stress (MPa)
dQ/dV (mAh cm-2 V-1)
Areal Capacity (mAh cm-2)

**Figure S7.** (a) Potential and stress of NFM111 electrode as a function of areal capacity showing different stages of stress during the 2$^{nd}$ cycle between 2- 4.1 V. (b) has the corresponding differential capacity (dQ/dV) plot.

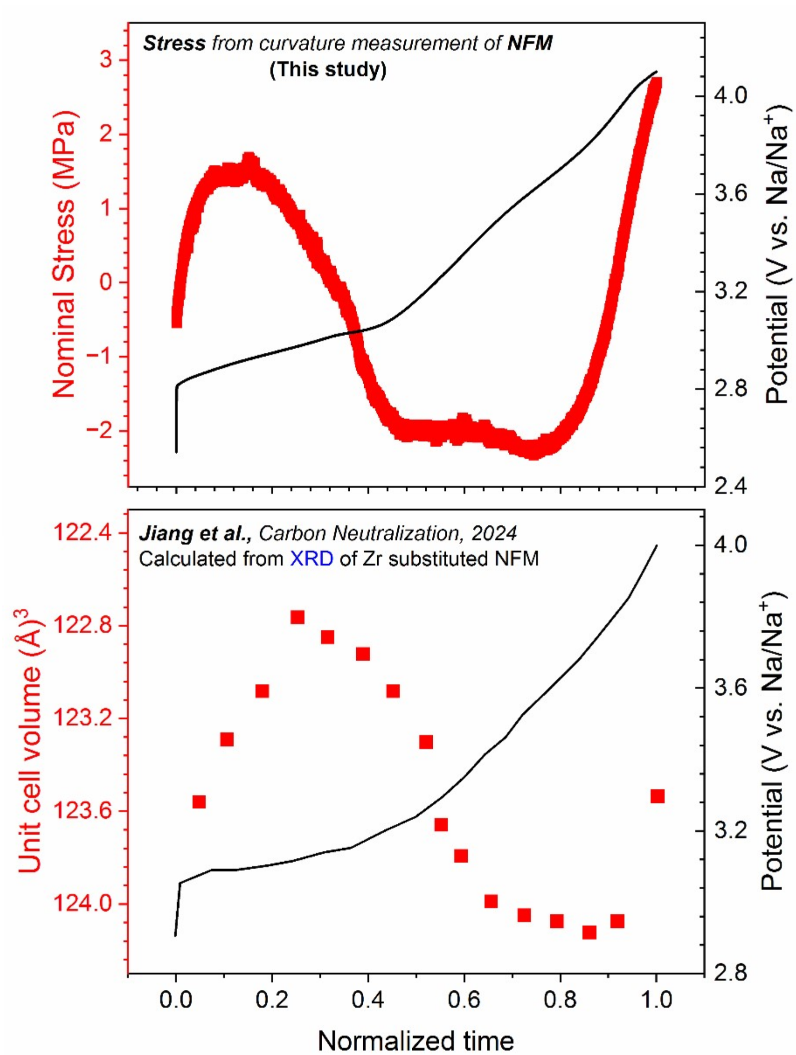



**Figure S8.** Comparison of stress data (from this study) with unit cell volume change from the research literature (Jiang et al., *Carbon Neutralization*, 2024 [2]) observed during $Na^+$ extraction from NFM electrode.

## References

(1) Freund, L. B.; Suresh, S. Thin Film Materials: Stress, Defect Formation and Surface

Evolution. *Cambridge Univ. Press* **2003**.

(2) Jiang, C.; Wang, Y.; Xin, Y.; Ding, X.; Liu, S.; Pang, Y.; Chen, B.; Wang, Y.; Gao, L. L.; Wu, F.; Gao, H. Toward High Stability of O3-type NaNi1/3Fe1/3Mn1/3O2 Cathode Material with Zirconium Substitution for Advanced Sodium-Ion Batteries. *Carbon Neutralization* **2024**, *3*, 233–244. https://doi.org/10.1002/cnl2.115.