Electronic Supplementary Information for

Revealing unusual storage failure of single-crystal high-nickel cathodes during high-temperature and high-humidity exposure

1. Experimental section

1.1 Sample Preparation

In this study, we used a pristine single-crystal high-nickel (SC-HN) material, where nickel makes up 88% of the total transition metal content. The precursor was prepared by a hydroxide co-precipitation process, in which metal sulfates and $NaOH/NH_3 \cdot H_2O$ were reacted under an inert atmosphere. This precursor was then thoroughly mixed with LiOH so that the lithium-to-transition-metal molar ratio was correct, plus an extra 5% lithium to make up for any loss during calcination. The mixture was heated in a tube furnace up to 880 °C in an O_2 environment, producing a black-gray powder that served as the fresh SC-HN material.[1]

1.2 Ambient Storage Scheme

To examine the stability and degradation of the SC-HN materials during storage, we split the as-prepared samples into several batches and stored them in air under high-temperature and high-humidity (HA) conditions. The storage environment was maintained at 50±1°C and about 80±5% relative humidity in a controlled temperature and humidity chamber. The samples were kept for different durations—0 day (fresh pristine material), 1 day, 7 days, 14 days, 21days, 28 days—labeled as P, 1D, 7D, 14D, 21D, and 28D, respectively. At the same time, we stored one sample at normal temperature and humidity (25℃-60%RH) for 1 day as a comparison sample, labeled 1D-NA. In the description of the data comparison, we label the previously mentioned 1D sample as 1D-HA to distinguish them.

1.3 Electrochemical measurements

Cathode electrodes were prepared by mixing 80 wt% active material, 10 wt% super carbon black, and 10 wt% polyvinylidene fluoride (PVDF) in NMP to form a slurry. The electrochemical performance

was evaluated using 2032-type coin cells. Each cell featured a lithium metal anode (14 mm in diameter), a single-layer Celgard2500 membrane as the separator, and 90 μL of electrolyte (1.0 M LiPF6 dissolved in EC/DEC at a 1:1 volume ratio), assembled in a glovebox under an argon atmosphere. Detailed procedures for electrode preparation and half-cell assembly are described in our previous works [2, 3]. The assembled cells were tested on a Landt CT3001A battery system.

2. Characterization

2.1 Synchrotron-based wide-angel X-ray scattering (WAXS)

Ex-situ wide-angel X-ray scattering (WAXS) tests were conducted at the National Synchrotron Radiation Research Center (NSRRC) using the electrode with Al foil as the current collector. The photon wavelength was set at 1.32 Å, and the exposure time for each scan was 60 seconds.

2.2 Scanning electron microscopy (SEM)

The morphological images of all the samples were taken with an equipment named CIQTEK SEM5000 operated at an accelerating voltage of 5-10 kV.

2.3 Transmission electron microscopy (TEM)

High-resolution transmission electron microscopy (HRTEM), atomic-resolution scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) images were performed with an FEI Titan G2 60-300 microscopy at 300 kV, which was equipped with a probe spherical aberration corrector.

2.4 Soft X-ray absorption spectroscopy (sXAS)

The local atomic environment and electronic configuration around the O and Ni atoms of all samples were investigated using soft X-ray absorption spectroscopy at the BL08U beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The O *K*-edge and Ni *L*-edge spectra were collected in both

total electron yield (TEY) and fluorescence yield (FY) modes, with the beam size of 150 mm × 50 mm.

[1] C. Yang, Y. Li, W. Su, X. Zhu, L. Hao, X. Wang, S. Wu, L. Chen, D. Cao, Y. Su, *J. Mater. Chem. A*. **2024**, 12, 20910-20920.

[2] Y. Li, X. Zhu, Y. Su, L. Xu, L. Chen, D. Cao, N. Li, F. Wu, *Small*. **2024**, 2307292.

[3] Y. Li, X. Zhu, C. Wei, Y. Fang, X. Wang, Y. Zhai, W. Kang, L. Chen, D. Cao, M. Wang, *Chin. Chem. Lett.* **2024**, 109536.

3. Supplementary figures

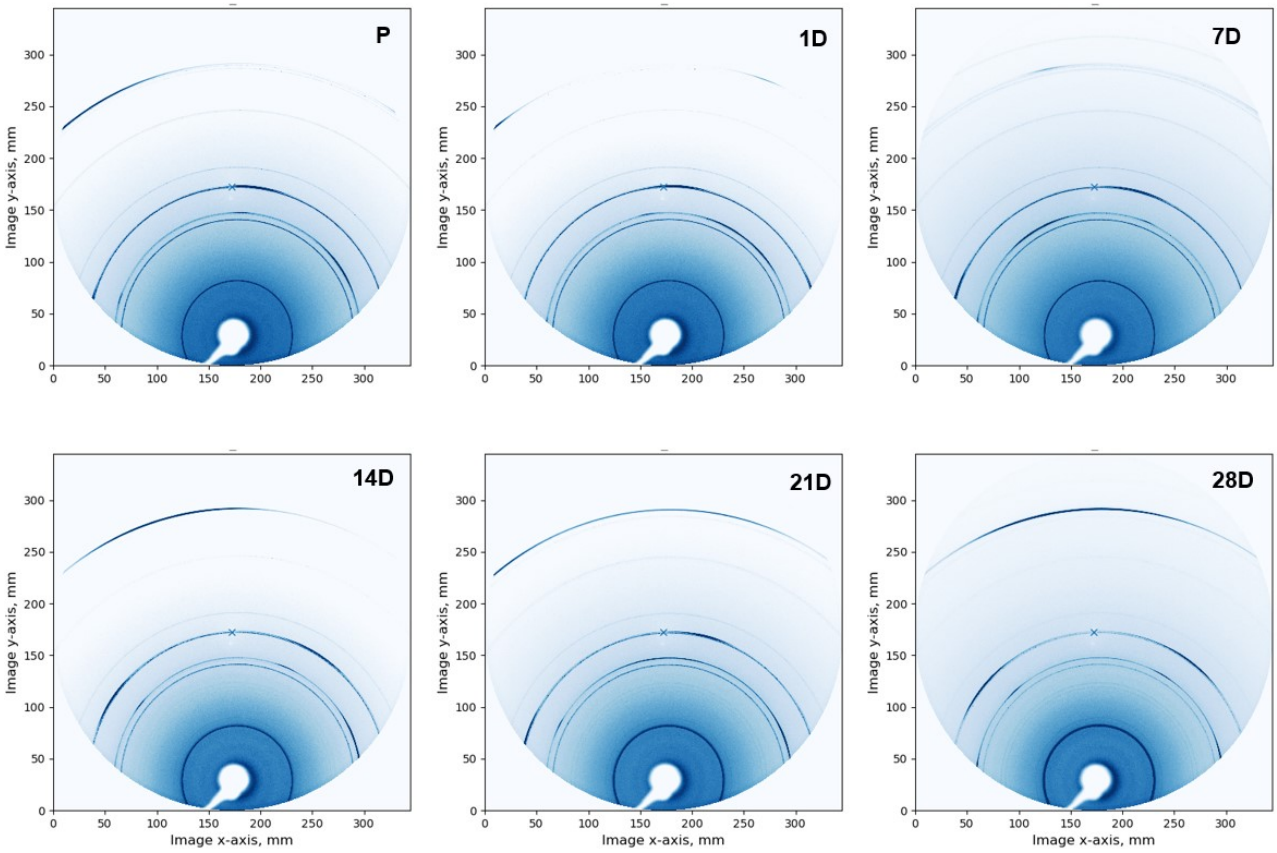

Figure S1 The Debye-Scherrer 2D counter plot (from synchrotron-based Wide Angle X-ray Scattering) of the samples stored for different durations (Pristine/P, 1D, 7D, 14D, 21D, 28D) in HA condition.

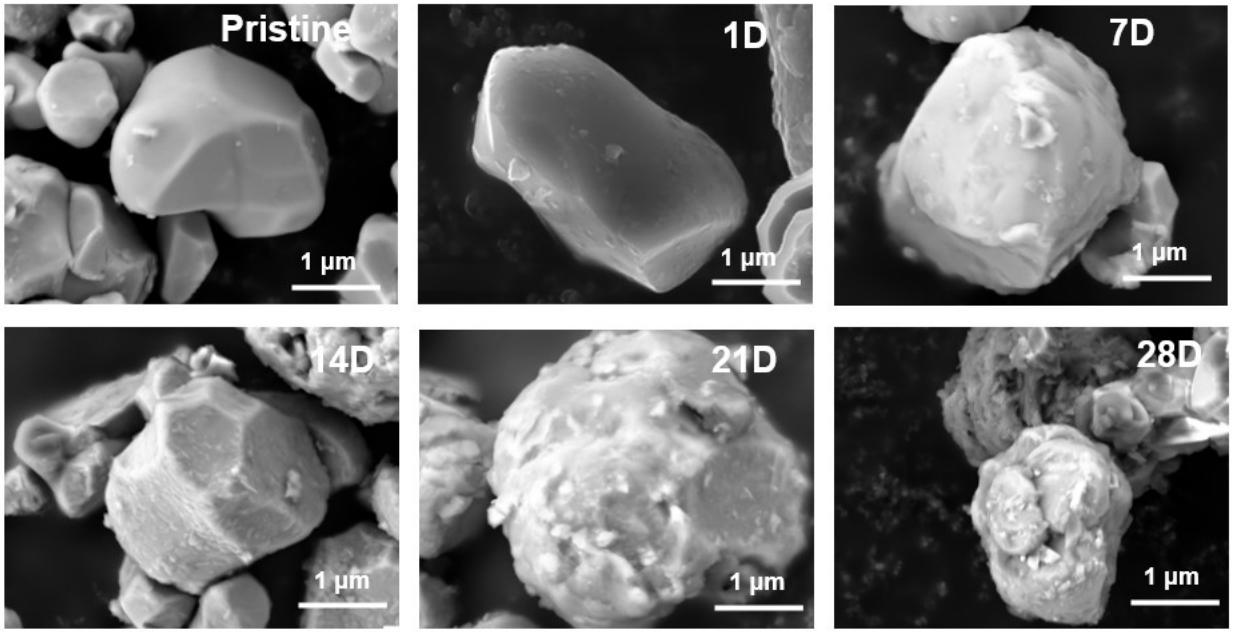

Figure S2 Scanning electron microscopy (SEM) images of the samples stored for different durations.

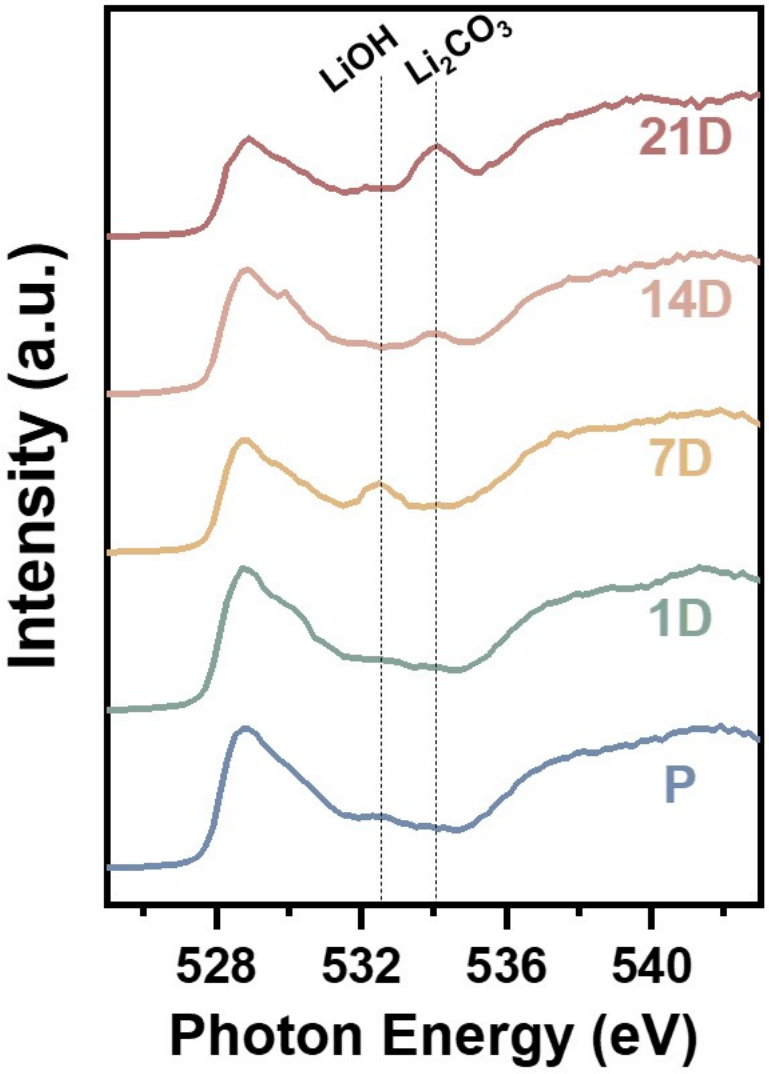

Figure S3 O K-edge FY mode of Synchrotron-based soft X-ray absorption spectra for the stored samples (P, 1D, 7D, 14D, 21D).

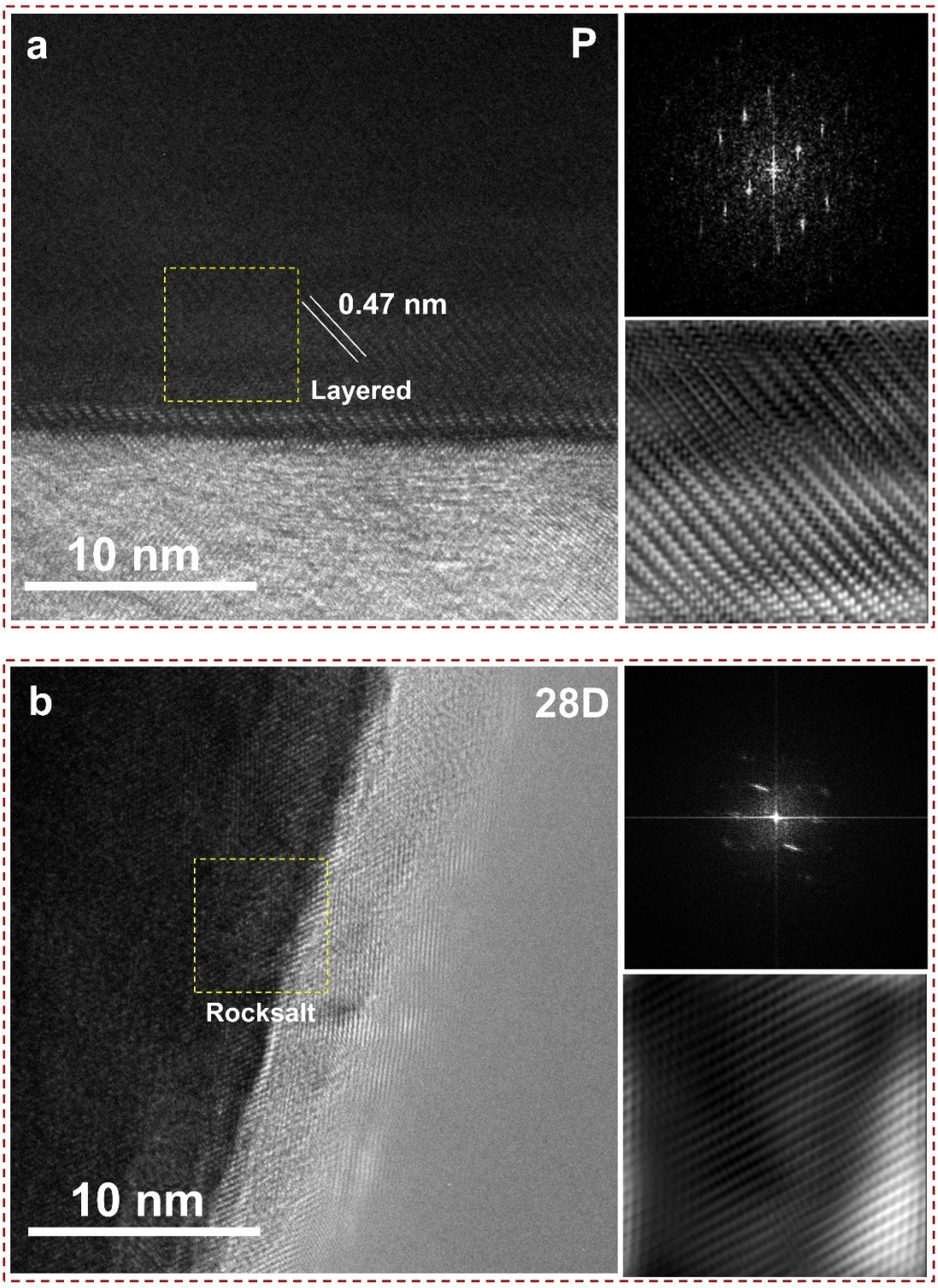

Figure S4 High-resolution TEM image of (a)sample P and (b)sample 28D are observed on the particle surface; the SAED correspond to the highlighted regions and the inverse FFT patterns.

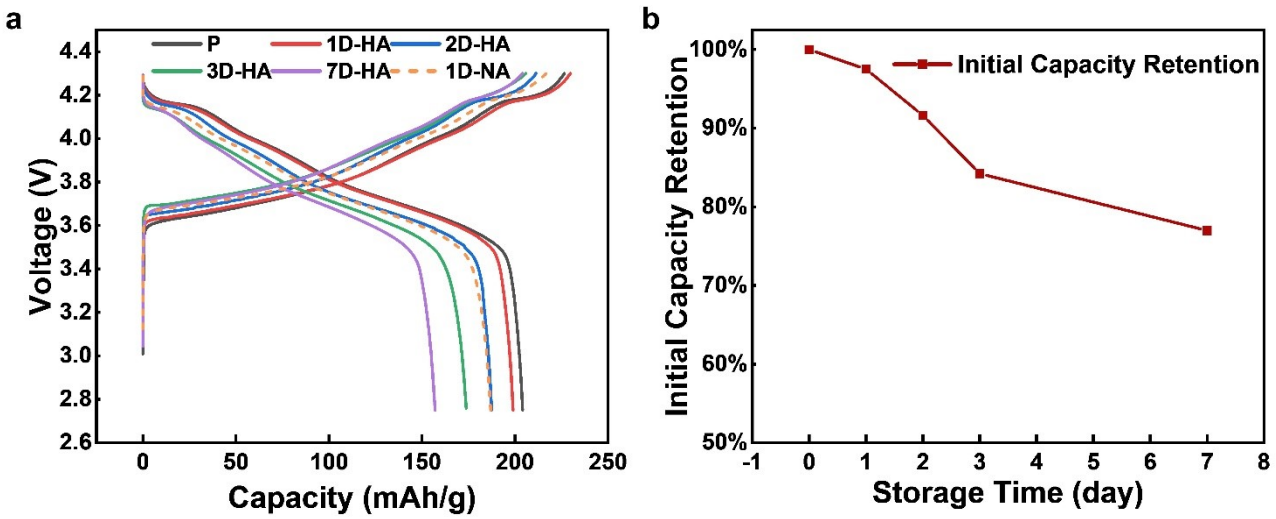

Figure S5 (a) Initial charge-discharge curves of sample P, 1D, 2D, 3D, 7D under HA condition storage and sample 1D under NA condition storage; (b) The initial discharge capacity retention with different storage samples.