Electronic Supplementary Material (ESI) for Energy Advances.

Supplementary Information: Probing Electrochemical Strain Generation in Sodium Chromium Oxide ($NaCrO_2$) Cathode in Na-ion Batteries during Charge/Discharge

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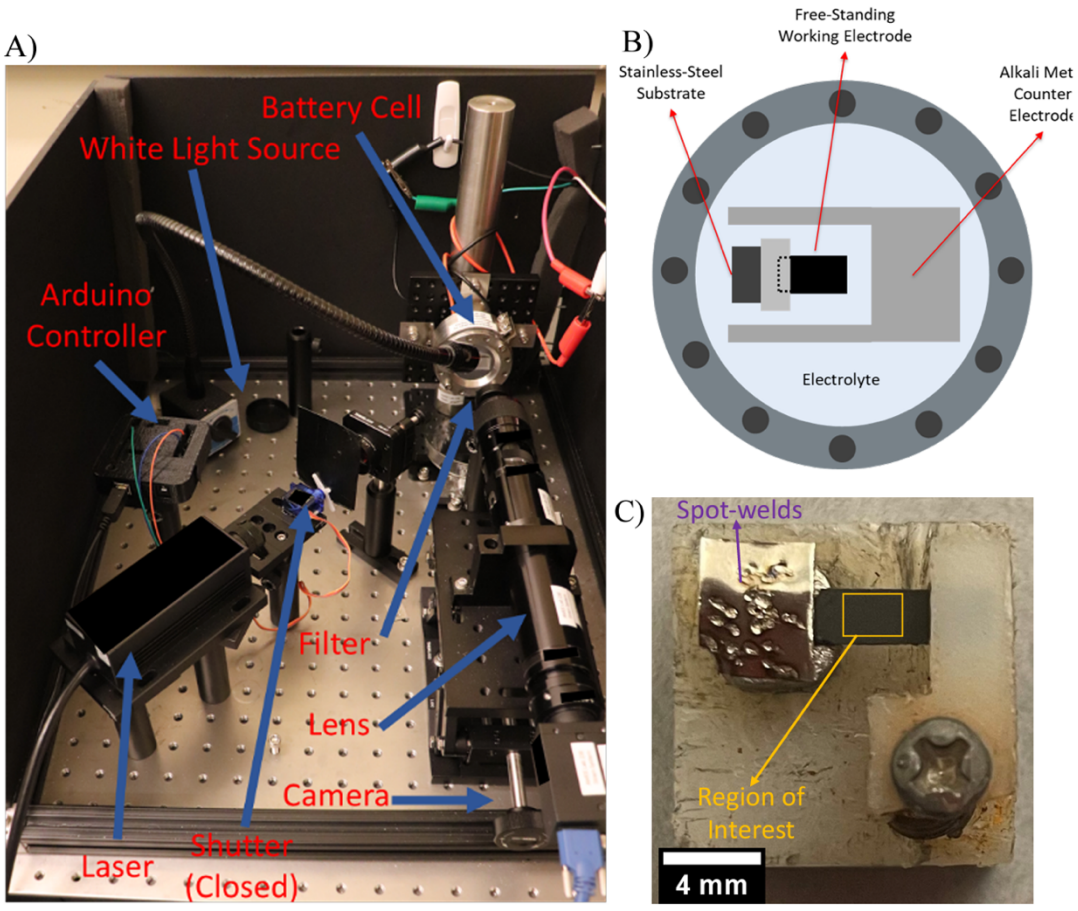
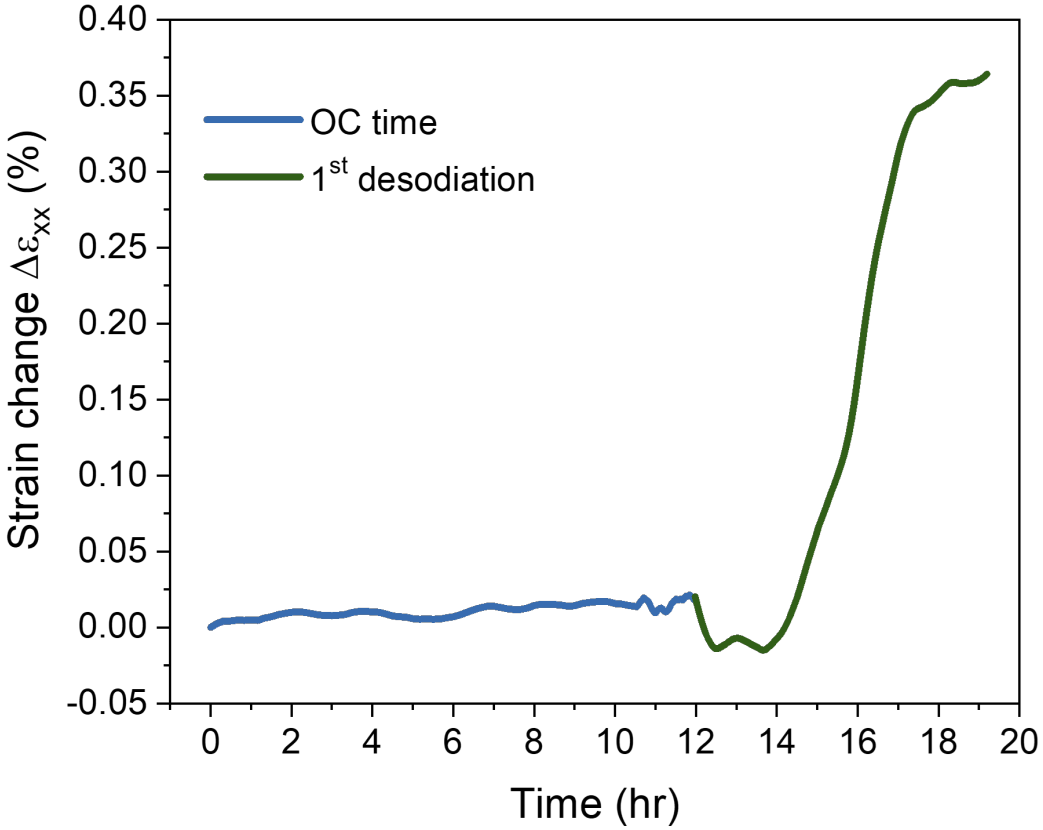
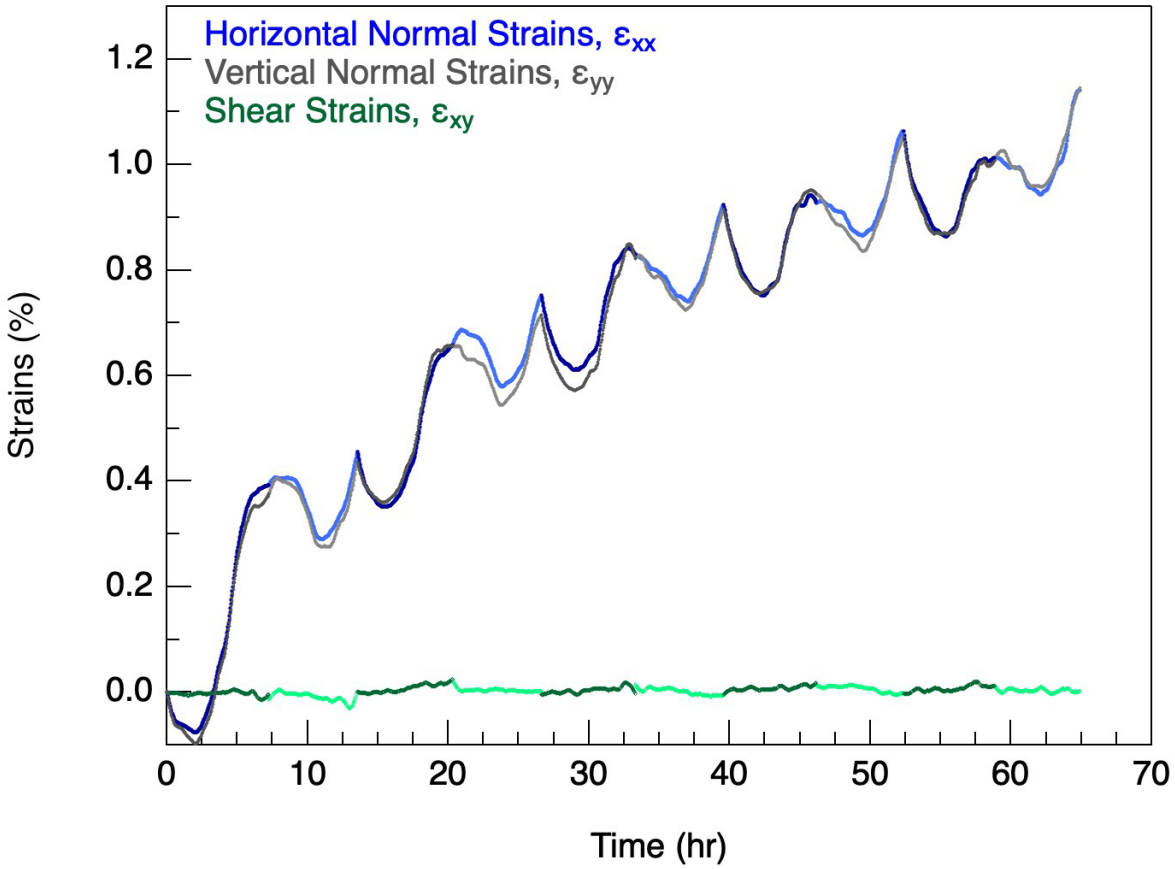
Strain Setup: A comprehensive description of the custom battery cell design and assembly is described in detail in our previous publication (Ozdogru et al., Nano Lett., 21, 18, 7579–7586, 2021). In this study, we employed an in-house-built custom experimental setup and a custom cell assembly designed for *operando* strain measurements (Supp. Figure 1A and B). The free-standing working electrode was placed onto a stainless-steel substrate using spot welding, with the electrode suspended from the substrate's edge, as shown in Supplementary Figure 1 (C). The working electrode, situated at the center of the custom cell assembly, was designed to capture the image throughout the electrochemical cycling process. The sodium metal used as a counter electrode was placed around the working electrode as shown in Supp. Figure 1B. The custom cell assembly was constructed of Polychlorotrifluoroethylene (PCTFE) sourced. Following the assembly process, the cell was enclosed with the quartz window to get optical access. And subsequently, the electrolyte filled cell was placed on the experimental setup for strain measurements.



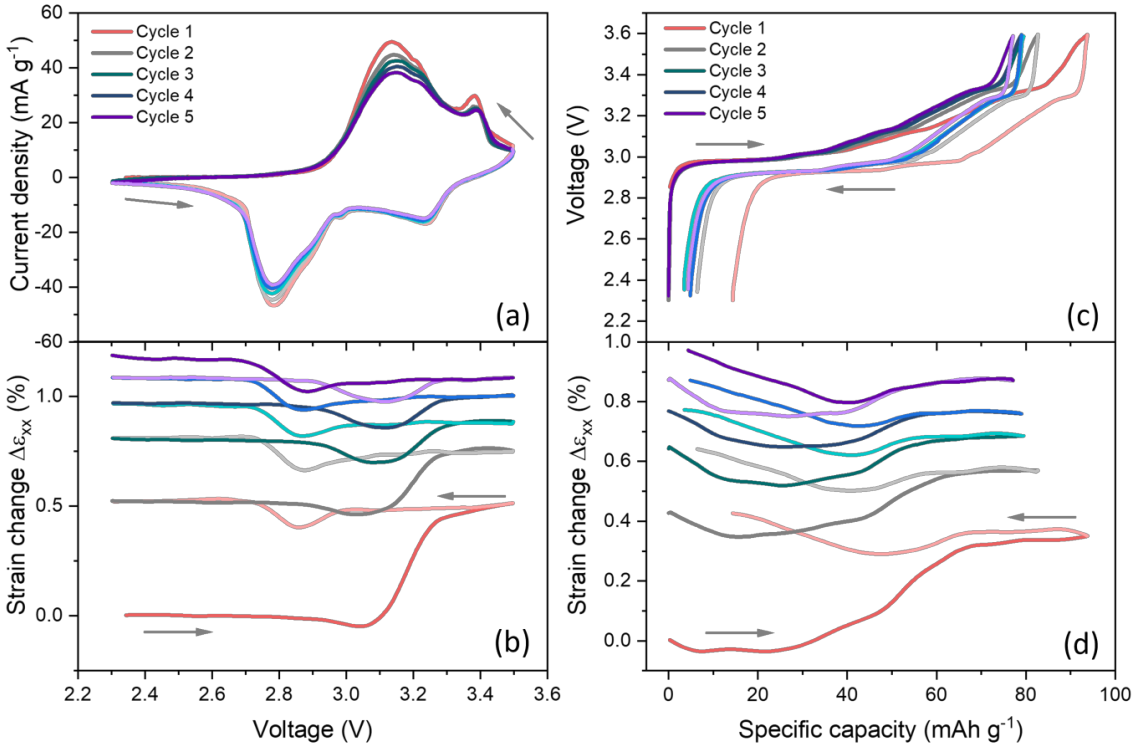
Supplementary Figure 1. The custom experimental arrangement for *operando* strain measurements (A) The picture of the experimental setup, (B) custom battery cartoon and (C) working-electrode spot-welded on the stainless-steel substrate (modified with permission from Ozdogru et al., Nano Lett., 2021)



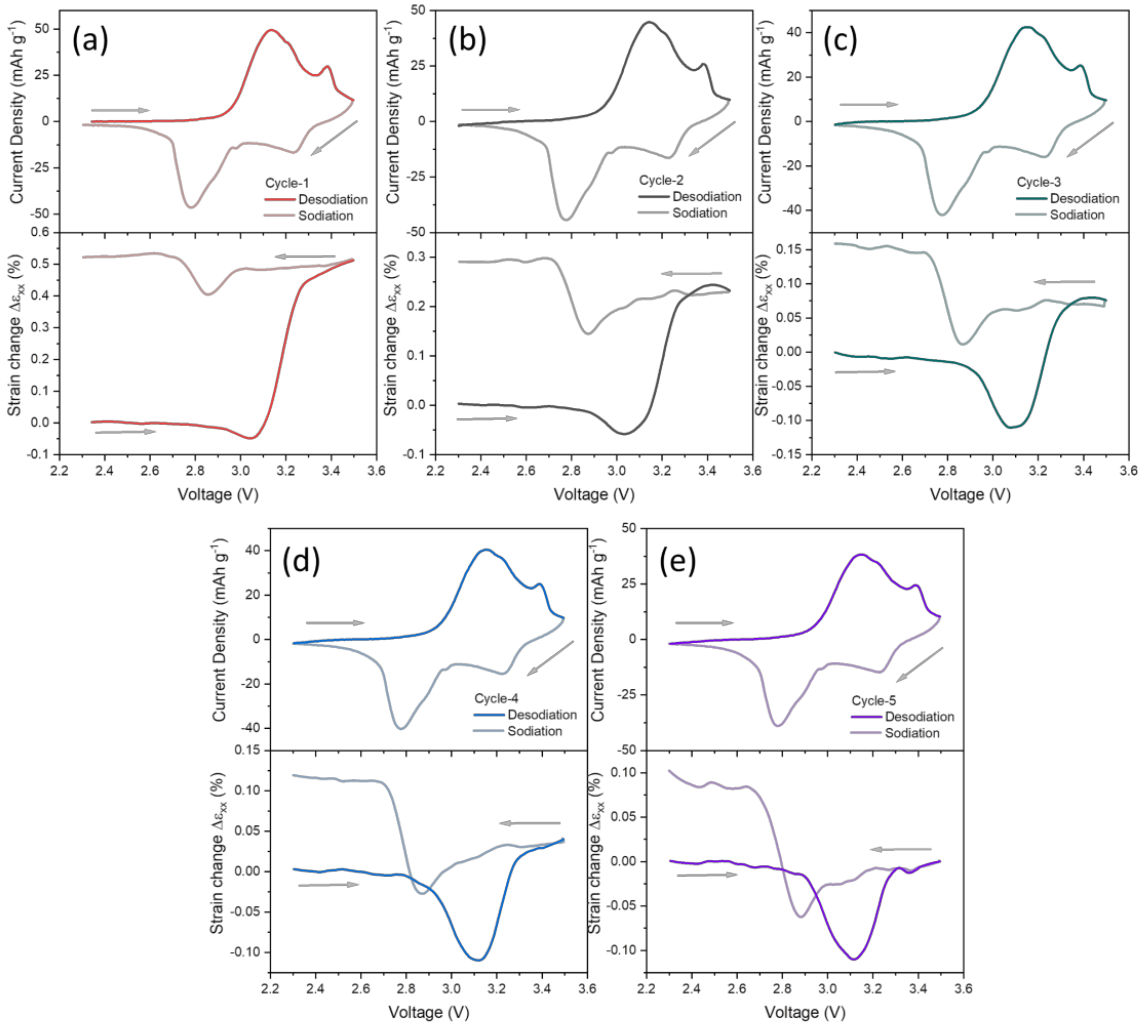
Supplementary Figure 2. Strain generation in the composite electrode during open circuit period and the subsequent first charge at C/25 rate.



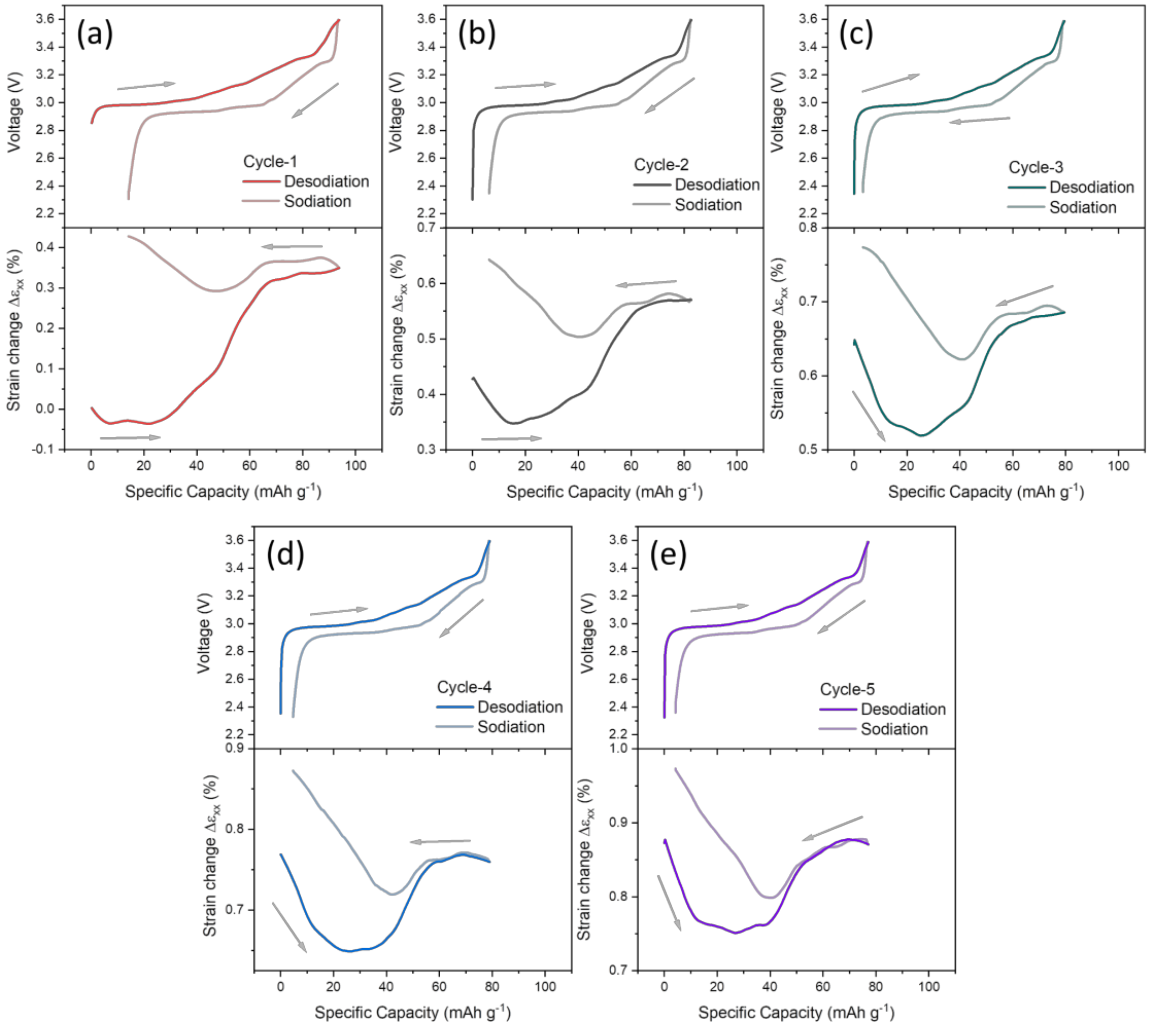
Supplementary Figure 3: Comparison of horizontal normal e_{xx} (blue lines), vertical normal e_{yy} (grey lines) and shear strains e_{xy} (green lines) in the composite electrode cycled at C/25 rate. Horizontal strains are from Figure 3 in the manuscript. Darker and lighter lines show charge and discharge, respectively.



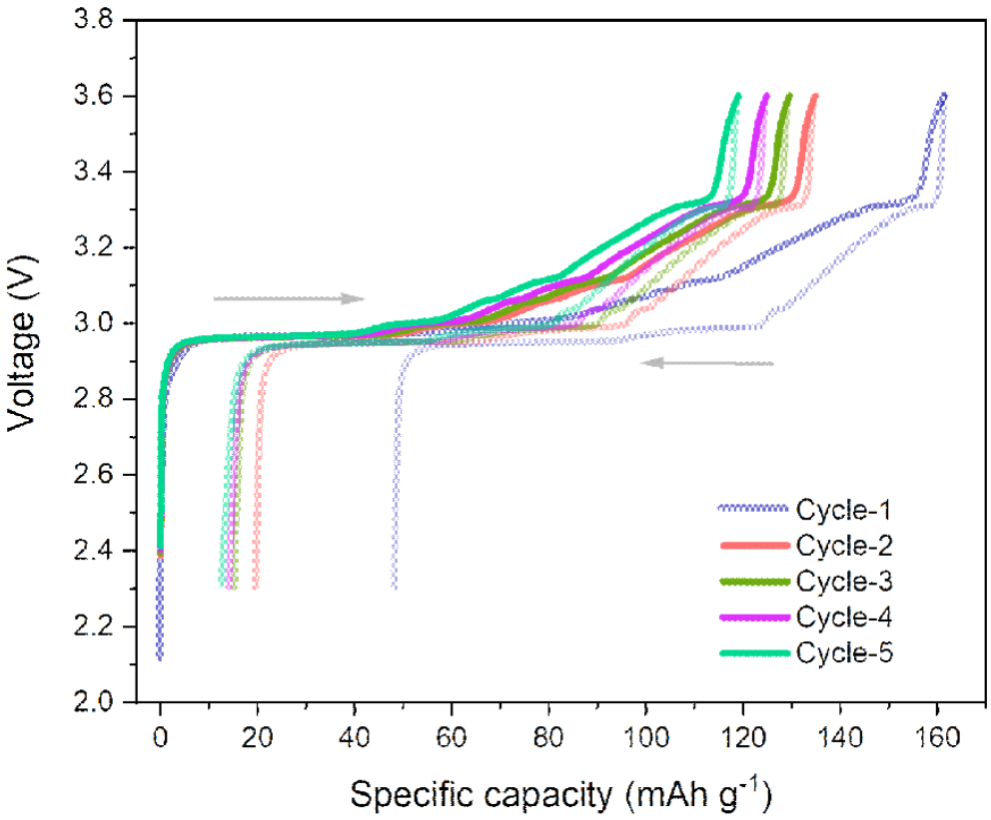
Supplementary Figure 4. a. The cyclic voltammetry of $NaCrO_2$ | Na cells from 2.3 to 3.5 V shows current density and b. corresponding strain generation in $NaCrO_2$ for the initial 5 cycles. c. the galvanostatic charge-discharge voltage profile and d. strain evolution of $NaCrO_2$ cathode during cycling between 2.3 V - 3.6 V for an initial five cycles.



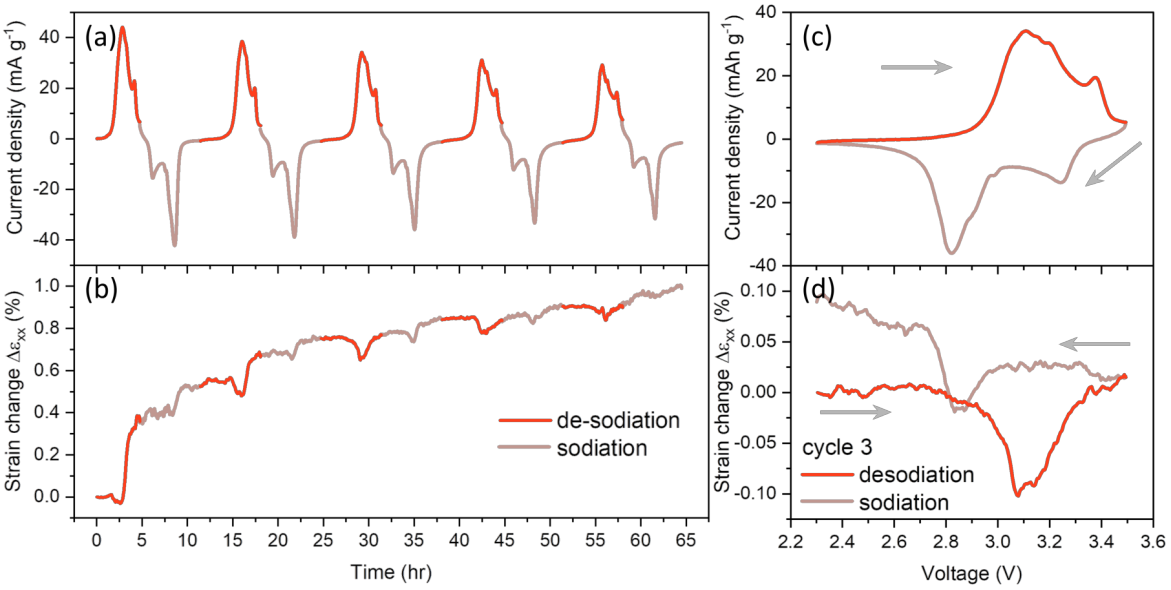
Supplementary Figure 5. (a-e) Current density and strain profile for each cycle from 2.3 V to 3.6 V in cyclic voltammetry at a scan rate of 50 μV/s.



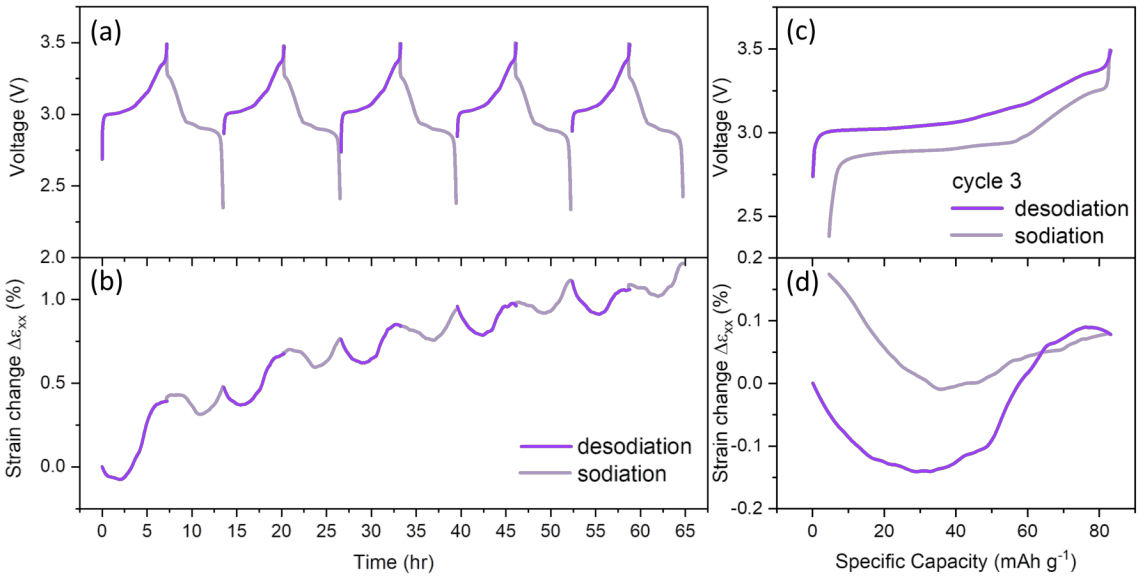
Supplementary Figure 6. (a-e) Voltage and strain profile for each cycle from 2.3 V to 3.6 V in galvanostatic cycling at current rate of C/25.



Supplementary Figure 7. Galvanostatic charge-discharge profiles of $NaCrO_2$ | Na in coin cell assembly cycled between 2.3 V to 3.6 V at C/25 current rate for initial 5 cycles.



Supplementary Figure 8. Repeated cyclic voltammetry experimental data (a) current density and (b) strain evolution of $NaCrO_2$ cathode w.r.t time at scan rate of 50 μV/s during cycling between 2.3 V - 3.5 V for initial five cycles. (c) current density and (d) strain evolution w.r.t voltage in the third cycle resetting strain to zero.



Supplementary Figure 9. Repeated galvanostatic cycling experimental data (a) voltage profile and (b) strain evolution of $NaCrO_2$ cathode during cycling between 2.3 V - 3.5 V for initial five cycles. (c) voltage profile and (d) strain evolution w.r.t specific capacity in the third cycle resetting strain to zero.