



# Excessive sodiation and desodiation of commercial NFM-hard carbon sodium-ion batteries induced by low-rate cycling

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## ABSTRACT

Experiments reveal that the electrodes of a commercial NFM || hard carbon sodium-ion battery undergo excessive sodiation and desodiation at low charge and discharge rates. These effects are observed during cycling, despite operating strictly within the manufacturer's recommended voltage limits of 1.5 V to 4.1 V. The resulting increase in charge capacity originates from an additional phase transition in the cathode active material, which manifests itself electrochemically as a voltage plateau that delays reaching the cut-off voltage during charging. The occurrence of the phase transition at high cell voltages is verified by operando X-ray diffraction measurements. During the subsequent discharge, the reverse transition takes place. Unusual deep discharge is enabled by the combination of low overpotentials and the characteristic potential profile of the cell. These phenomena are reproducibly observed across multiple test sequences. To separate the effects of the individual electrodes on this full cell behavior, harvested electrodes from a commercial cell are assembled into an experimental three-electrode setup and analyzed by differential voltage analysis. Since the high-voltage phase transition is reported to involve irreversible processes, adapting characterization and cycling protocols (especially voltage limits) may improve long-term performance and facilitate future analyses.

## 1. Introduction

The sodium-ion battery (SIB) is considered a drop-in technology for the predominant lithium-ion battery (LIB). Both technologies use porous electrode designs with liquid electrolytes and can be produced with the same equipment and manufacturing processes [1]. SIB raw materials are characterized by lower marginal costs [2], lower criticality, better availability and wider geographical distribution [3,4]. SIB's comparably lower specific and volumetric energy density makes them specifically interesting for small- to medium-range vehicles and stationary storage systems.

Recent studies on commercial SIBs, particularly those employing  $\text{Na}_x\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NFM) cathodes and hard carbon (HC) anodes, have revealed substantial deviations from LIBs in terms of electrochemical behavior. Although energy densities already exceed  $160 \text{ Wh kg}^{-1}$  [5], comparable to those of LFP-based LIBs, notable limitations emerge under real-world cycling conditions. Specifically, SIBs exhibit significant increases in internal resistance and efficiency losses at low state of

charge (SoC), particularly below 30 %, where voltage hysteresis, nonlinear overpotentials and kinetic limitations, primarily caused by the HC anode, dominate the cell behavior. Unlike LIBs, which maintain stable efficiency across the full SoC range, SIBs perform significantly better when cycled between 50 % and 100 % SoC. [6,7] While necessary due to sodium's inability to intercalate into graphite, HC introduces its own challenges [8]. Sodium storage occurs via a combination of adsorption on the surface, intercalation, and pore filling, but slow kinetics at low potential can contribute to heterogeneous sodium deposition. Several studies have reported irreversible sodium plating as a side reaction under such conditions [9–11]. NFM-based cathode materials offer significant potential for sodium-ion batteries due to their high specific capacity and cost-effectiveness. However, structural instabilities during repeated charge–discharge cycles, particularly phase transitions and volume changes, pose considerable challenges by inducing mechanical stress and accelerated cathode degradation [12,13]. Based on the cells and electrodes examined, our results show that SIBs exhibit distinct electrochemical characteristics and respond differently to conventional

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constant current (CC) charging and discharging protocols with varied C-rates. We present experimental evidence of an additional phase transition at high voltages discovered in a commercial NFM || HC cell that affects both its available capacity and longevity.

## 2. Experimental

The experiments are conducted using commercial 18650 SIBs from HAKADI, a battery brand of Selian Energy, with a nominal capacity of 1.5 A h. The cells employ NFM as the cathode and HC as the anode active material [6,14]. According to the manufacturer's datasheet the specified operating voltage range spans from 1.5 V to 4.1 V, with charge and discharge currents limited to 1C and 3C respectively. The cycling protocols are carried out using a BaSyTec CTS Lab XL system at a controlled temperature of 25 °C, maintained by a Binder MK115 climate chamber.

First, the cell is discharged at a C-rate of C/2, until the lower voltage limit of 1.5 V is reached. Following this, three pseudo-open-circuit-voltage (pOCV) curves are obtained by charging the cell at C/20 to 4.1 V and then discharging at the same rate to 1.5 V. Afterwards, three CC charge–discharge cycles at a rate of 1C within the voltage window of 1.5 V to 4.1 V are performed. The combined sequence of pOCV measurement and subsequent cycling is performed twice. The corresponding voltage profile is shown in Fig. 1(a).

For subsequent process assignment, using differential voltage analysis (DVA), experimental cells are constructed to attribute the observed effects separately to the anode and cathode. The active material is extracted from a fresh full cell in a glove box under argon atmosphere. Circular electrode disks with a diameter of 18 mm are punched from the electrode sheets and are assembled in a laboratory test cell setup (EL-Cell ECC-PAT-Core). Anode and cathode disks are separated by a Whatman GF/A glass fiber separator with a sodium reference ring to measure the half-cell potentials. The electrolyte consists of 80  $\mu\text{L}$  of 1M NaPF<sub>6</sub> in EC:DMC (1:1). To ensure homogeneous distribution of the electrolyte, the assembled cells are rested for at least twelve hours in a climate chamber, which is maintained at 25 °C by a Huber CC-515 circulation thermostat, under argon atmosphere. All following tests are carried out under these ambient conditions using a Biologic VMP300 potentiostat. The cells undergo two C/5 formation cycles, followed by a single C/2 cycle to determine their capacity. Based on the measured capacity, each cell is then cycled in the same way as the commercial full cell.

For the operando X-ray diffraction (XRD) measurement a customized CR2032 coin cell with a 6 mm quartz glass window (100  $\mu\text{m}$  thickness) is used. Circular electrode disks with a diameter of 14 mm for the anode and 13 mm for the cathode are punched from the commercial cells electrode sheets. Anode and cathode disks are separated by a Whatman GF/A glass fiber separator. As electrolyte 100  $\mu\text{L}$  of 1M NaPF<sub>6</sub> in EC:DMC (1:1) is added. Galvanostatic (dis-)charge cycling was performed in a voltage range of 1.5 V–4.1 V at C/20 (= pOCV). XRD patterns were collected in transmission in the Stoe StadiP diffractometer every 15 min in a range of  $0^\circ \leq 2\theta \leq 36.5^\circ$  with a step size of  $0.015^\circ$ .

### 3. Results and discussion

The charge and discharge capacities of the 18650 cell for pOCV and 1C cycling are shown in Fig. 1(b). As expected, higher capacities are obtained at the lower C-rate. Notably, under pOCV conditions, the discharge capacity of the first pOCV cycle exceeds the corresponding charge capacity. Furthermore, the charging capacity at 1C is approximately 6% higher directly after the pOCV cycle compared to the subsequent 1C cycles. Therefore, the Coulombic efficiencies during and after the pOCV cycle exhibit a transient deviation. As shown in Fig. 1(c), the efficiency exceeds 100% during the first pOCV cycle, and stabilizes close to 100% in the subsequent two pOCV cycles. A

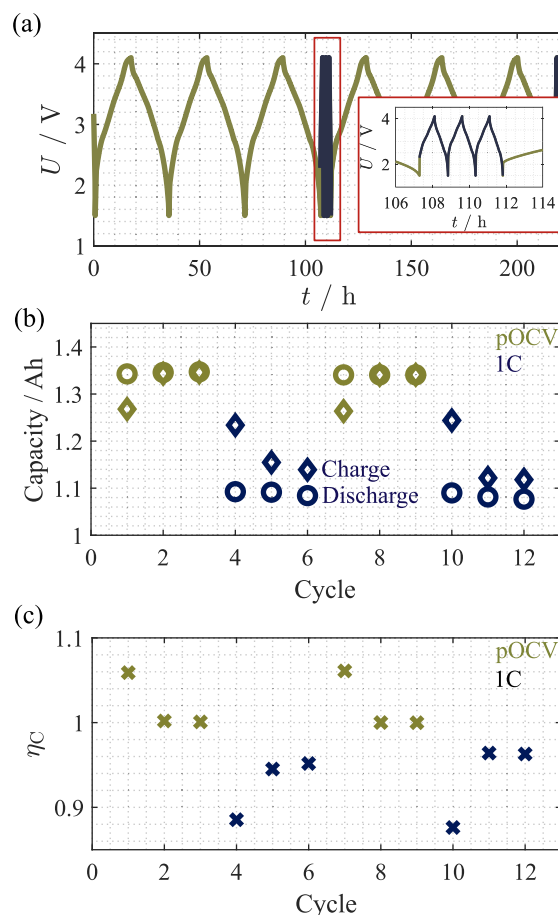


**Fig. 1.** The voltage profile obtained during the three-cycle experimental protocol of the commercial 18650 sodium-ion cell is shown in (a), whereas the corresponding charge and discharge capacities are presented in (b), and the Coulombic efficiencies in (c). In (a), a magnified view of the 1C cycles is provided in the inset, with the zoomed region indicated in red. In (b), discharge and charge capacities are indicated by circles and diamonds, respectively. In (b) and (c), pOCV capacities and efficiencies are displayed in olive, and 1C capacities and efficiencies in blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

marked decline to below 89 % is observed in the first cycle after the C-rate is increased to 1C. In the following 1C cycles, the efficiency stabilizes again at approximately 95 %. To investigate the origin of the observed variations in Coulombic efficiency and charge capacity, DVA is performed on the third (last) pOCV and the subsequent three 1C cycles. As shown in Fig. 2(c) and (d) for the respective charge and discharge processes, this approach enables the identification of subtle electrochemical changes, such as phase transitions, kinetic limitations, or side reactions.

To reduce noise and enhance the clarity of the DVA signal, a moving average filter is applied using the MATLAB function *movmean*. A window size of 4 is used for the 1C curves, while a size of 50 is applied to the pOCV curves. For both experiments a sampling rate of 10 s is employed. To facilitate comparison of the DVA curves, they are horizontally aligned along the capacity axis. Specifically, a uniquely identifiable peak in the charge and discharge curves of each cycle is aligned with the corresponding peak in the pOCV reference curve. Due to the differing total capacities discussed earlier, this alignment can produce apparent negative capacity values, which arise directly from the applied shift.

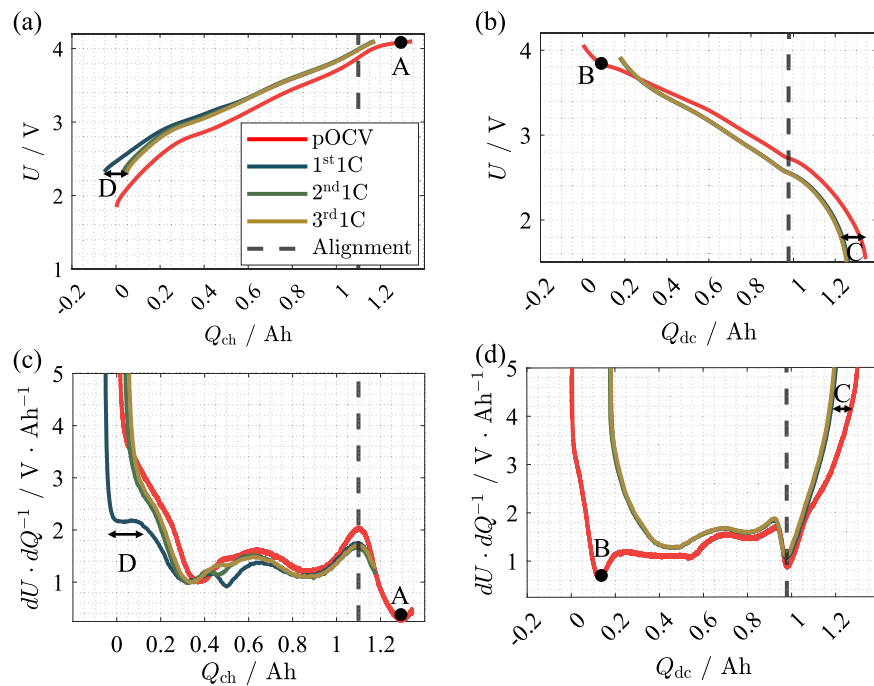


**Fig. 2.** Voltage profile of the third pOCV and the following three 1C charge (a) and discharge (b) cycles of the 18650 cell. The pOCV cycles are shown in red, while the 1C cycles are colored in blue, green and gold. Differential voltage analysis in (c) and (d). All curves are aligned to the characteristic peak in the differential voltage curve of the pOCV cycle used as reference, to better compare the different C-rates. This shift can lead to apparent negative values of the charge. Characteristic features are marked with capital letters. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

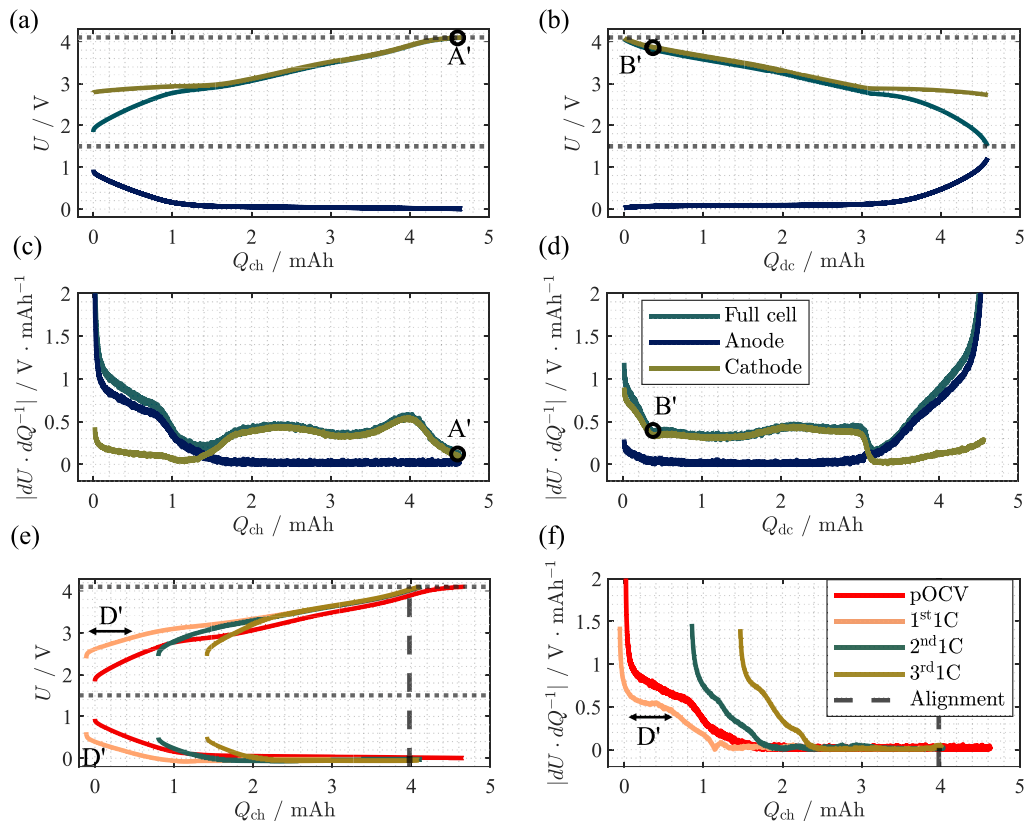


**Fig. 3.** Voltage curves and differential voltage analysis of charging (a) and (c) and discharging (b) and (d) cycles at a pOCV current rate, showing the differential voltages of the anode, cathode, and full cell in a three electrode setup. The curves are shown in their original form; no peak alignment has been applied. The dotted horizontal lines indicate the voltage limits of the full cell. In (e), the full cell voltage and the anode potential of the third pOCV cycle together with the following three 1C charging cycles are presented. In (f), the corresponding differential voltage curves of the anode for these cycles are shown, and characteristic features equivalent to those of the 18650 cell are marked with capital letters. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



in literature, the cathode phase transition at high voltages causes structural degradation of the cathode [12,13] and should therefore be avoided to ensure long-term cell stability and performance. These effects may arise from poor cell balancing or suboptimal voltage limits, yet their presence in commercial cells makes them directly relevant for practical applications. Therefore, choosing lower cut-off voltages before the phase transition may offer better cycling stability. However, the key factors influencing the onset of the phase transition, such as temperature and C-rate, remain to be investigated in the context of the intended, application-specific load profiles and the manufacturer's operational limits.

## CRediT authorship contribution statement

**Tom Rüther:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Andrea Kinberger:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Niklas Feistel:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Data curation. **Matteo Bianchini:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis. **Michael A. Danzer:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

Data will be made available on request.

## References

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