Superior Sodium Storage Properties in the Anode Material NiCr$_2$S$_4$ for Sodium-Ion Batteries: An X-ray Diffraction, Pair Distribution Function, and X-ray Absorption Study Reveals a Conversion Mechanism via Nickel Extrusion

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The pseudo-layered sulfide NiCr$_2$S$_4$ exhibits outstanding electrochemical performance as anode material in sodium-ion batteries (SIBs). The Na storage mechanism is investigated by synchrotron-based X-ray scattering and absorption techniques as well as by electrochemical measurements. A very high reversible capacity in the 500th cycle of 489 mAh g$^{-1}$ is observed at 2.0 A g$^{-1}$ in the potential window 3.0–0.1 V. Full discharge includes irreversible generation of Ni$^0$ and Cr$^0$ nanoparticles embedded in nanocrystalline Na$_2$S yielding shortened diffusion lengths and predominantly surface-controlled charge storage. During charge, Ni$^0$ and Cr$^0$ are oxidized, Na$_2$S is consumed, and amorphous Ni and Cr sulfides are formed. Limiting the potential window to 3.0–0.3 V an unusual nickel extrusion sodium insertion mechanism occurs: Ni$^{2+}$ is reduced to nanosized Ni$^0$ domains, expelled from the host lattice, and is replaced by Na$^+$ cations to form O3-type like NaCrS$_2$. Surprisingly, the discharge and charge processes comprise Na$^+$ shuttling between highly crystalline NiCr$_2$S$_4$ and NaCrS$_2$ enabling a superior long-term stability for 3000 cycles. The results not only provide valuable insights for the electrochemistry of conversion materials but also extend the scope of layered electrode materials considering the reversible nickel extrusion sodium insertion reaction as a new concept for SIBs.

1. Introduction

Rechargeable batteries are an essential part of electrical energy storage (EES) for our modern society as the technological demand rises rapidly since the last two to three decades.\cite{8–11} The climate change and the pollutant impact of fossil fuels as prime power supply raised a major interest in large-scale EES of clean, renewable and sustainable, in short, green energy from, e.g., solar, wind or geothermal sources to overcome the variation in energy production and consumption.\cite{6,7} Commercialized full cell rechargeable battery types are commonly Li-based (lithium-ion batteries (LIBs)) and widely utilized for mobile electric applications like portable electronics and electric vehicles.\cite{8,7} Owing to the uneven distribution of Li in the earth crust with the highest abundances in geopolitically critical areas of the planet and relatively high costs for Li production make LIBs less suitable for large-scale EES applications.\cite{8–11} This is one important reason why an indispensable research topic is dedicated to identify abundant, economic, environmentally friendly and efficient alternatives. Sodium-ion batteries (SIBs) have received enormous attention in the last few years to address this matter due to the high abundance of Na and a promising high theoretical energy density of SIBs.\cite{2,11–18} The electrochemical and physical properties of Na are comparable to Li. But in contrast to Li$^+$ or K$^+$, the electrochemical insertion of Na$^+$ into untreated graphite is hindered and new anode materials for SIBs with high capacity, cycle stability and fast charge–discharge capability must be discovered.\cite{19–22} Among the various anode materials investigated for the application in SIBs, transition metal sulfides (TMSs) attracted high interest due to their abundance, low costs and high theoretical capacities.\cite{31–27} Beyond the intercalation/deintercalation mechanism using layered electrode materials, which is operating in most commercial LIBs, the so-called conversion reaction has become a research focus due to the promising high energy densities and specific capacities.\cite{34,28,29} During the electrochemical Na uptake in TMSs, the metal cations are reduced to metallic...
nanoparticles embedded in a Na2S matrix. However, conversion reactions are accompanied by large volume changes leading to contact loss to the current collector often resulting in poor cyclability. Different strategies are pursued to compensate the unfavorable volume change, e.g., heterostructure design and organic coatings (such as SnSe2/ZnSe@polydopamine). Nanoengineering or design of carbon hybrid materials using reduced graphene oxide (rGO), carbon nanofibers, or carbon nanotubes. But most of these carbon-based additives are too expensive for large-scale applications.

Ternary TMSs demonstrated good performances as anode materials in SIBs. But to continue development, prescient concepts might be necessary to face the obstacles of conversion-type and intercalation-based materials in SIBs. Recently, we discovered the formation of crystalline Na0.7Cu0.15CrS2 during the sodiation process in the pseudo-layered compound CuCrS2 via copper extrusion sodium insertion mechanism. Hereby, nanosized Cu particles are expelled from a [CrS2] host lattice dramatically enhancing the cycle stability of CuCrS2 compared to mere NaCrS2. This discovery raised two indispensable questions: i) do other ternary layer-like Cr sulfides exhibit comparable electrochemical properties and ii) can a transition metal extrusion from a pseudo-layered host material be exploited to reversibly shuttle Na+ cations with structural retention of the host lattice? This could provide a new concept for SIBs using particular transition metal atoms for Na insertion/extraction in layer-like electrode materials. During our search for pseudo-layered TMSs we identified NiCr2S4 as a suitable candidate exhibiting a high theoretical capacity (736.9 mAh g–1) assuming a full conversion reaction of Ni2+ and Cr3+ ions to their elemental states as formally shown in Equation (1)

NiCr2S4 + 8 Na+ + 8 e− → Ni0 + 2Cr0 + 4 Na2S

Only few investigations on Cr sulfides for the application in SIBs were reported, like, e.g., NaCrS2 and NaCr2/3Ti1/3S2 as cathode materials. The electronic, structural, and thermoelectric properties of NiCr2S4 have been studied but this is the first report about the electrochemical performance of this material as an anode material for SIBs. The investigation of fundamental electronic and structural changes during the Na uptake and release is a prerequisite topic to understand and improve electrochemical alkali-metal storage properties. Thus, we performed synchrotron-based ex situ high-energy powder X-ray diffraction (PXRD), total-scattering X-ray experiments to calculate pair distribution functions (PDFs), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy during the electrochemical Na uptake and release in NiCr2S4. Additionally, the electrochemical performance and electrokinetic characteristics were analyzed via galvanostatic discharge–charge (GDC) cycling, cyclic voltammetry (CV) and galvanostatic intermittent titration technique (GITT).

Herein, we report the discovery of an unusual nickel extrusion sodium insertion mechanism in the early stage of Na uptake in NiCr2S4. Ni2+ ions can be reversibly extruded/inserted from vacancy layers followed by redox processes to form nanocrystalline fcc-Ni and NaCr2S4. This Na+ shuttle via crystalline phases yields an outstanding long cycle life for 3000 cycles at 2.0 A g–1. On the other hand, higher reversible capacities can be obtained by sacrificing cycle stability if Na/NiCr2S4 cells are discharged to full conversion accompanied by irreversible decomposition of the host lattice via reduction of Cr3+ ions to generate ultra-small Cr0 domains and nanocrystalline fcc-Ni embedded in nanocrystalline Na2S.

2. Results and Discussion

2.1. Characterization of Pristine NiCr2S4

The stoichiometry of the title compound was determined with a scanning electron microscope (SEM) by energy-dispersive X-ray (EDX) spectroscopy and elemental analysis (Figure S1, Note S1, Tables S1 and S2, Supporting Information), yielding the composition of Ni1.00(7)Cr1.95(8)S4.03(5). Additionally, the layered nature is apparent in a SEM image of the pristine product (Figure S2, Supporting Information). The as-synthesized NiCr2S4 crystallizes in the monoclinic space group (SG) I2/m (CrS2 type, Figure 1a). The result of a joint Rietveld PXRD (Figure 1b) and Rietveld-like least-squares refinement of PDF data (Figure 1c) evidence very good phase purity with minute amounts of NiS (~1.1 wt%) and Cr2O3 (~0.5 wt%) as impurities, with the latter presumably resulting from reaction of Cr with the quartz amouple. We note that the impurities could only be detected using high-energy synchrotron radiation but not with standard laboratory PXRD. The results can be regarded as a hint that one should be cautious claiming phase purity using in-house PXRD data. The joint refinement demonstrates a nearly perfect match of the averaged long-range and local structure, and the structural parameters (Table 1) are close to values reported in the literature. Small deviations in the fit of G(r) (1–5 Å, Figure 1c) could result from high atomic motion correlations at short distances. The CrS2 type structure can be described as an ordered defect variant intermediate between the NiAs and CdI2 structures, comprising CrS2 slabs formed by edge-sharing CrS6 octahedra (fully occupied layers) and 50% of octahedral sites in layers between the CrS2 slabs is occupied by Ni2+ (vacancy layers), leading to a pseudo-layered structure type.

2.2. Cycle and Rate Performance in SIBs

Figure 2a shows selected GDC profiles recorded during the first 100 cycles applying a current rate of 0.1 A g–1 (0.14C) for the first and 0.5 A g–1 (0.68C) for all subsequent cycles. During the first discharge, the voltage drops linearly to 0.9 V and subsequently to 0.3 V until about 3 Na are inserted in NiCr2S4, followed by an extensive pseudo-plateau located between 0.3 and 0.25 V. After uptake of about 8 Na per formula unit, the voltage decreases steadily to the cut-off potential of 0.1 V and a high total initial discharge capacity of 900 mAh g–1 (~9.8 Na/NiCr2S4) is obtained. A capacity of 647 mAh g–1 (~70 Na/NiCr2S4) is recovered in the first charge process. The irreversible capacity loss (~28%) is caused by chemical side-reactions and formation of a solid electrolyte interphase (SEI, see also Section 2.3), which was also observed for, e.g., CuV2S4 and NiCo2S4.
The GDC profiles are very similar in every subsequent cycle after the second one and demonstrate a highly reversible process. The cycle performance of Na/NiCr$_2$S$_4$ at 0.5 and 2.0 A g$^{-1}$ (2.71C) is shown in Figure 2b. Applying 0.5 A g$^{-1}$, the capacity drops by 11% from 606 mAh g$^{-1}$ (=6.6 Na/NiCr$_2$S$_4$) in the second to 539 mAh g$^{-1}$ (=5.9 Na/NiCr$_2$S$_4$) in the 100th cycle, presumably due to contact loss to the current collector resulting from volume changes, which are inevitable for conversion-type materials especially microcrystalline compounds. Subsequently, a slight increase of capacity to 558 mAh g$^{-1}$ (=6.1 Na/NiCr$_2$S$_4$) is observed until cycle 200. Applying a higher current rate of 2.0 A g$^{-1}$, the electrode shows a tremendous long-life cycle performance and delivers a capacity of 489 mAh g$^{-1}$ (=5.3 Na/NiCr$_2$S$_4$) even after the 500th cycle, before the capacity steadily drops during subsequent cycling. The outstanding high capacities are accompanied with excellent Coulombic charge efficiencies of >99% after the third cycle applying 0.5 or 2.0 A g$^{-1}$. The rate capability of a Na/NiCr$_2$S$_4$ cell was also tested at various current rates between 0.1 and 5.0 A g$^{-1}$. Figure 2c,d display selected GDC curves at various current rates and the rate performance test, respectively. The highly reversible character of the electrochemical reaction even at high current rates is demonstrated by unchanged voltage profiles during the GDC processes (Figure 2c). In the first cycles and at low current rates (0.1 to 0.5 A g$^{-1}$), the capacity decreases slightly as already observed at a constant current (CC) rate of 0.5 A g$^{-1}$ (Figure 2b). However, the Na/NiCr$_2$S$_4$ cell demonstrates a superior rate-stability especially at higher current rates delivering tremendously high capacities (Table 2) and the Na/NiCr$_2$S$_4$ cell even retains 65% (399 mAh g$^{-1}$) at 5.0 A g$^{-1}$ compared to the capacity obtained at 0.1 A g$^{-1}$. After high rate testing, when current density is reduced to the initial value of 0.1 A g$^{-1}$, the NiCr$_2$S$_4$ electrode delivers a capacity of 583 mAh g$^{-1}$, corresponding to a loss of only 5% resulted by the rate capability test. Hence, the Na/NiCr$_2$S$_4$ cell is in good condition and reveals an excellent reversibility between high and low current rates.

Selected electrochemical Na storage properties of NiCr$_2$S$_4$ are highlighted and compared to similar sulfidic anode materials utilized in SIBs in Table 3. The large operating voltage range of Na/NiCr$_2$S$_4$ cells is an unfavorable property and a common disadvantage for conversion-based electrodes (see Table 3). Even so, the rate capability and capacity retention of Na/NiCr$_2$S$_4$ cell is in good condition and reveals an excellent reversibility between high and low current rates.

![Figure 1. a) Monoclinic structure of the title compound NiCr$_2$S$_4$, co-refined by b) Rietveld method of the PXRD pattern and c) Rietveld-like least-squares approach of the PDF data. Refinement details are listed in Table 1.](image)

**Table 1.** Structural parameters for pristine NiCr$_2$S$_4$ from PDF–PXRD joint refinement. SG: $I12/m1$, $a = 5.90354(6)$ Å, $b = 3.41113(4)$ Å, $c = 11.09825(12)$ Å, $\beta = 91.3065(9)$. Quantitative phase analysis (PXRD): 98.4 wt% NiCr$_2$S$_4$, 0.5 wt% Cr$_2$O$_3$, 1.1 wt% NiS. $R_{wp}$ (PXRD) = 2.54%, $R_{wp}$ (PDF) = 11.0%, strain: $e = 4.3(1) \times 10^{-4}$.

| Atom | WP$^{a}$ | $x$ | $y$ | $z$ | DW$^{b}$ [Å$^2$] | SOF$^{c}$ |
|------|---------|----|----|----|----------------|--------|
| Cr1  | 4i      | 0.02051(7) | 0.0 | 0.23915(4) | 0.544(9) | 0.999(2) |
| Ni1  | 2c      | 0.0 | 0.0 | 0.5 | 0.561(11) | 0.975(1) |
| S1   | 4i      | 0.32895(13) | 0.0 | 0.38085(6) | 0.630(7) | 1.0 |
| S2   | 4i      | 0.34210(14) | 0.0 | 0.86600(7) | 0.630(7) | 1.0 |

$^{a}$WP = Wyckoff position; $^{b}$DW = Debye–Waller factor; $^{c}$SOF = site occupancy factor.
cells are outstanding compared to CuCrS₂, [39] NiCo₂S₄, [53, 55, 56] NiS, [57] Ni₃S₄, [58, 59] or NiS₂. [60, 61] The superior electrochemical performance of the title compound is even more remarkable considering the crystallinity of the title compound and that any highly conductive and costly additives like rGO could be avoided in contrast to most reports about nanocrystalline hybrid materials for application in SIBs, e.g. nanocrystalline NiCo₂S₄/rGO. [53]

2.3. Sodium Storage Mechanism

Discharge and charge processes were stopped at distinct points in the first cycle as shown in GDC profile in Figure 3b and electrodes were recovered at these points for PXRD, PDF analysis (Section 2.3.1) and X-ray absorption spectroscopy (XAS, Section 2.3.2) to elucidate the Na storage mechanism schematically shown in Figure 3a. Differing capacities observed in the first cycle during electrochemical performance tests (Figure 2a, ≈ 9.8 Na/NiCr₂S₄ at 0.14C) and in the present curve (Figure 3b, ≈ 8.1 Na/NiCr₂S₄ at 0.05C) is caused by usage of polyvinylidene difluoride (PVDF) in the former tests, while the latter was recorded without PVDF. PVDF and/or additives like fluoroethylene carbonate contribute to SEI formation by decomposition considering the crystallinity of the title compound and that any highly conductive and costly additives like rGO could be avoided in contrast to most reports about nanocrystalline hybrid materials for application in SIBs, e.g. nanocrystalline NiCo₂S₄/rGO. [53]

Table 2. Results of rate performance test.

| Current rate [A g⁻¹] | C-rate | Capacity [mAh g⁻¹] | Capacity retention [%] |
|----------------------|--------|--------------------|-----------------------|
| 0.1                  | 0.14C  | 612                | 100                   |
| 0.2                  | 0.27C  | 579                | 95                    |
| 0.5                  | 0.68C  | 550                | 90                    |
| 0.7                  | 0.95C  | 534                | 87                    |
| 1.0                  | 1.36C  | 521                | 85                    |
| 1.5                  | 2.04C  | 505                | 83                    |
| 2.0                  | 2.71C  | 492                | 80                    |
| 3.0                  | 4.07C  | 468                | 76                    |
| 5.0                  | 6.78C  | 399                | 65                    |
| 0.1                  | 0.14C  | 583                | 95                    |

*a) Every tenth cycle; b) Related to the first rate. 

Figure 2. Performance of Na/NiCr₂S₄ test cells in the potential window 3.0–0.1 V: a) selected GDC curves at a current density of 0.1 and 0.5 A g⁻¹ for the first and subsequent cycles, respectively; b) cycling performance and Coulombic charge efficiency applying current densities of 0.5 and 2 A g⁻¹; c) GDC profiles at various current rates recorded during d) rate performance test and Coulombic charge efficiency.
to NaF in SIBs.\textsuperscript{11,62,63} This is evidenced by a PXRD pattern collected for a discharged sample containing only PVDF and Super C65 carbon (Figure S3, Supporting Information) exhibiting mainly Bragg reflections of NaF.

### 2.3.1. Investigation of the Storage Mechanism with PXRD and PDF

Results of high-energy PXRD (Figure 4a) and PDFs (Figure 4b,d) allow a detailed study of changes in the short- and long-range order occurring during the GDC processes. The first discharge can be divided into two regions I and II (compare Figure 3b). During uptake of 2 Na/NiCr$_2$S$_4$ (region I) corresponding to the steady voltage drop to about 0.3 V in the GDC profile (Figure 3b), Ni$^{2+}$ ions are reduced to fcc-Ni (green dashed lines in Figure 4a) and simultaneously a new intermediate phase is formed. Interatomic Ni–Ni distances in fcc-Ni can be clearly assigned to appearing peaks in the PDFs for 0.5 to 2 Na/NiCr$_2$S$_4$ (green dashed lines in Figure 4b). The transformation of NiCr$_2$S$_4$ into an intermediate phase is indicated by appearance of additional reflections, most clearly seen at 1.81°\textsuperscript{2θ} for 0.5 Na/NiCr$_2$S$_4$. In the structure of O3-NaCrS$_2$ (SG: $\overline{3}Rm$, Figure S5, Supporting Information) the $c$-axis represents the interlayer distance. A closer look at the (003) reflection (Figure S6, Supporting Information) of the NaCrS$_2$ related intermediate (abbreviated as int-NaCrS$_2$) reveals an increase from $d = 6.46$ to 6.54 Å in region I close to the value for mere bulk O3-NaCrS$_2$ ($d_{(003)} = 6.50$ Å).\textsuperscript{64,65}

#### Table 3. Selected electrochemical Na storage properties of NiCr$_2$S$_4$ and comparable sulfidic anode materials in SIBs.

| Anode material          | Theoretical capacity [mAh g$^{-1}$] | Cycling stability: capacity [mAh g$^{-1}$/current [mA g$^{-1}$]/cycle number | Rate capability: capacity [mAh g$^{-1}$/current [mA g$^{-1}$]/cycle number | Operating voltage range [V] | Reference                  |
|-------------------------|-------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|-----------------------------|-----------------------------|
| Bulk NiCr$_2$S$_4$       | 736.9                               | 558/500/200                                                                      | 492/2000                                                                         | 3.0–0.10                    | This work                   |
| Bulk CuCrS$_2$          | 596.7                               | 420/600/100                                                                      | 158/2000                                                                         | 2.5–0.10                    | [39]                        |
| Nano-NiCo$_2$S$_4$/rGO  | 703.4                               | 388/100/300                                                                      | 325/1500                                                                         | 3.0–0.01                    | [53]                        |
| Nano-NiCo$_2$S$_4$      | 703.4                               | 387/1000/60                                                                     | 217/2000                                                                         | 2.8–0.01                    | [55]                        |
| NiCo$_2$S$_4$           | 703.4                               | 580/100/50                                                                       | 413/2000                                                                         | 3.0–0.30                    | [56]                        |
| NiS/rGO                 | 590.6                               | 483/200/100                                                                      | 372/2000                                                                         | 3.0–0.01                    | [57]                        |
| Nano-Ni$_3$S$_4$/rGO    | 704.5                               | 460/1000/200                                                                     | 390/2000                                                                         | 2.8–0.05                    | [58]                        |
| Nano-Ni$_3$S$_4$/C      | 704.5                               | 297/1000/100                                                                     | 230/2000                                                                         | 3.0–0.01                    | [59]                        |
| Nano-Ni$_3$S$_4$/p-CNF\textsuperscript{41} | 872.9                               | 371/100/200                                                                      | 300/2000                                                                         | 3.0–0.01                    | [60]                        |
| Ni$_3$S$_4$ nanospheres | 872.9                               | 319/500/1000                                                                     | 420/2000                                                                         | 2.9–0.40                    | [61]                        |

\textsuperscript{41}p-CNF = porous carbon nanofibers.

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Figure 3. a) Schematic illustration of the Na storage mechanism elucidated for NiCr$_2$S$_4$ by ex situ investigations at distinct points highlighted in (b), the GDC profile of the first cycle recorded with powder cells.
Reflections corresponding to NiCr$_2$S$_4$, fcc-Ni and int-NaCrS$_2$ are broad and partially superimposed, preventing a more detailed analysis. But interatomic distances for O3-NaCrS$_2$ shorter than $\approx 6$ Å can be clearly assigned to peaks in the PDF, while longer distances (marked with grey asterisks in Figure 4b) are not observed suggesting that int-NaCrS$_2$ is nanocrystalline. Rietveld-like modeling of the PXRD pattern and PDF (2 Na/NiCr$_2$S$_4$) considering different stacking like the O1-, P2-, P3- and P3’-types reported for deintercalation phases of, e.g., Na$_{x}$Cr$_{2/3}$Ti$_{1/3}$S$_2$,\cite{42} did not result in reasonable fits. Summarizing, a description of the long-range order of int-NaCrS$_2$ is not possible with the present data because multiple factors, like, e.g., presence and type of stacking faults, shape and size of coherently scattering domains, degree of strain, degree of Na$^+$ occupation and the possibility of remaining Ni atoms in int-NaCrS$_2$. Additionally, antisite occupation as previously reported for deintercalated NaCrS$_2$\cite{41} cannot be excluded. To shed more light on the nature of int-NaCrS$_2$, a sample after uptake of 2 Na/NiCr$_2$S$_4$ was heated at 400 °C under inert conditions. In the PXRD pattern of the product (Figure S7, Supporting Information), all reflections to O3-NaCrS$_2$ are present indicating that the intermediate phase int-NaCrS$_2$ is related to the known layered structure polymorph. In summary, the chemical reaction in region I (compare Figure 3a, left) is expressed by Equation (2)

$$\text{NiCr}_2\text{S}_4 + 2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{NaCrS}_2 + \text{Ni}^0 \quad (2)$$

In region II (2 to 8 Na/NiCr$_2$S$_4$), the position of the (003) reflection remains unchanged, suggesting that no further Na$^+$ ions are inserted (Figure 4a and Figure S6, Supporting Information), but int-NaCrS$_2$ is successively decomposed, as evidenced by decreasing reflection intensities, and for $\geq 3$ Na/NiCr$_2$S$_4$ reflections of Na$_2$S are observed (dashed purple line in Figure 4a). Additionally, the intense PDF peak of the Cr–Cr distance at $\approx 3.5$ Å (Figure 4c) of int-NaCrS$_2$ decreases significantly. This conversion process occurs in the pronounced pseudo-plateau observed in the first discharge (Figure 3b). After full discharge (8 Na/NiCr$_2$S$_4$) the presence of nanocrystalline...
fcc-Ni and Na$_2$S is evidenced by whole powder modeling (WPPM)\cite{66} with volume weighted average domain sizes of $D_{\text{vol-Ni}} \approx 5$ nm and $D_{\text{vol-Na}_2\text{S}} \approx 4$ nm (compare Figure S8, Note S3, and Table S3, Supporting Information) and this result is supported by related peaks in the PDF (dashed green and purple lines in Figure 4c). In contrast to the product after the first discharge, Na$_2$S domain sizes are too small for reliable WPPM after the second discharge, whereas a comparable fcc-Ni domain size is estimated ($D_{\text{vol-Ni}} \approx 8$ nm).

2.3.2. Investigation of the Storage Mechanism with XAS at Ni and Cr K-edges

XANES spectra and corresponding first deviations $d\mu(E)_{\text{norm}}/dE$ of samples collected during the first cycle and of reference samples are shown in Figure 5. The Cr K-edge of NiCr$_2$S$_4$ (Figure 5a) is located at 5995.8 eV, an intense signal for the $1s \rightarrow 4p$ transition at 5999.0 eV and a pre-edge feature with low intensity at 5989.2 eV. The latter is a dipole forbidden but quadrupole allowed $1s \rightarrow 3d$ transition for an absorber in a centrosymmetric environment. These observations are in line with the oxidation state Cr$^{3+}$ and an octahedral coordination by sulfur anions, and similar features are observed for Cr$_2$S$_3$ containing Cr$^{3+}$ and Cr$_6$ octahedra.

After uptake of 1 Na/NiCr$_2$S$_4$ (region I), the XANES spectrum remains almost unchanged, indicating that no reduction of Cr$^{3+}$ ions occurred. For 1.5 and 2 Na/NiCr$_2$S$_4$ a very small edge energy shift of $\approx 0.5$ eV to lower values is observed. This shift may be explained by i) a superposition of Cr$^{2+}$ and Cr$^{3+}$ (compare Cr$_2$S$_3$ and Cr$_6$S$_8$ in Figure 5a) and/or ii) by very small domains because spectral features of nanoparticles in XANES do not match with those observed in well crystalline reference samples.\cite{67} In any case, a closer look at $d\mu(E)_{\text{norm}}/dE$ (Figure 5a, right inset) evidences comparable Cr K-edge contributions in reference O3-NaCrS$_2$ and the intermediate observed at 1.5 and 2 Na/NiCr$_2$S$_4$ (blue arrows in Figure 5a, left inset) very similar to those found for O3-NaCrS$_2$ (dashed orange in Figure 5a). Moreover, the intense $1s \rightarrow 4p$ transition located at 5999.1 eV is nearly unchanged compared to that for pristine Cr$_2$S$_3$. During further Na uptake in region II (Figure 5b) the Cr K-edge shifts to lower energy and the $1s \rightarrow 4p$ transition decreases, while simultaneously the feature at 5989.0 eV increases finally resembling that of bcc-Cr (8 Na/NiCr$_2$S$_4$). Differences between the spectrum and that for Cr foil are due to the nanocrystalline, disordered or even amorphous nature of Cr in the electrode. The reduction process is accompanied by an isosbestic point around $\approx 5995$ eV evidencing a single-step-reaction mechanism in region II, which is in line with observations from PXRD (see Section 2.3.1).

The Ni K-edge of NiCr$_2$S$_4$ (Figure 5c) at 8339.9 eV and the signal of the $1s \rightarrow 4p$ transition at 8343 eV are typical for Ni$^{2+}$ in octahedral geometry. Successive Na uptake is accompanied with a decrease of the signals and the $1s \rightarrow 4p$ transition is comparable to that of elemental fcc-Ni. This reduction from Ni$^{2+}$ to Ni$^0$ occurs in a single reaction step in region I and II since the XANES spectra change around an isosbestic point at $\approx 8338.5$ eV. Linear combination fitting (details in Note S4, Table S4, and Figure S11, Supporting Information) reveals the main reduction ($\approx 70\%$) of Ni$^{2+}$ during uptake of 2 Na/ NiCr$_2$S$_4$ and indicates an incomplete Ni extrusion in region I, most likely due to slow reaction kinetics.

A comparison of XANES spectra at the Cr K-edge of a discharged (0.1 V) and charged product (3.0 V) indicates the oxidation of Cr$^0$ to Cr$^{3+}$ in region III as the edge energy and pre-edge feature shift to 5995.4 and 5989.0 eV, respectively, and the $1s \rightarrow 4p$ transition at 5999 eV reappears (Figure 5d). These features cannot unambiguously assigned to a distinct Cr sulfide because these exhibit similar XANES features (compare Figure 5d, inset). However, the Cr K-edge energy is closer to that of Cr$_2$S$_3$ than Cr$_2$S$_4$, indicating that the averaged valence state of Cr is slightly lower than +3 in the charged sample. A comparison of XANES spectra at the Ni K-edge of a charged product (3.0 V) and that of h-NiS points to formation of Ni$^{2+}$ in region III due to an almost ideental edge energy and pre-edge
feature (Figure 5e), while small differences are caused by the nanosized nature of Ni$_2^+$ sulfide.

The evolution of pseudo-radial distribution functions (pRDFs) $|\chi(R)|$ during the first cycle is displayed in Figure 6a,b for the Cr and Ni absorber, respectively. Fitting results of pRDFs are presented in Figure 6c,d for 2 Na/NiCr$_2$S$_4$ (see Figure S13, Supporting Information, for corresponding EXAFS $\chi(k)$ fits), whereas results for NiCr$_2$S$_4$ (Figure S14, Supporting Information), 8 Na/NiCr$_2$S$_4$ (Figure S15, Supporting Information), after charge to 3.0 V (Figure S16, Supporting Information) and details (Note S5 and Table S5, Supporting Information) are compiled in the Supporting Information. According to the refinement of crystallographic data of NiCr$_2$S$_4$ (see Section 2.1) all NiS$_6$ (vacancy layers) and CrS$_6$ (fully occupied layers) are distorted. A fit of EXAFS data using the complex monoclinic structure as a model would result in too many independent parameters for the Nyquist criterion.$^{[68]}$ Reasonable parameters for NiCr$_2$S$_4$ ($R$-value of 0.002) were obtained applying a simplified model as explained in the Supporting Information (see Note S5, Supporting Information) yielding short-range distances comparable to values calculated from crystallographic data (see Table S6, Supporting Information).

During Na uptake in region I, a peak at $\approx$3.2 Å appears in the pRDFs of Cr (Figure 6a), which points to a transition from low symmetry for NiCr$_2$S$_4$ indicated by a nearly flat pRDF beyond the first coordination shell to higher symmetry for 2 Na/NiCr$_2$S$_4$. A fit using O3-NaCrS$_2$ as model (Figure 6c, $R$-value of 0.004) yields good agreement of the local structure with distances of

Figure 5. a–e) XANES spectra at Cr K-edge (a,b,d) and Ni K-edge (c,e) at selected states during the first cycle and of reference samples. The bottom right insets display the first deviations $d\mu(E)$norm/$dE$; the left inset in (a) is a magnification of pre-edge features for NiCr$_2$S$_4$ (black), 2 Na/NiCr$_2$S$_4$ (blue), and O3-NaCrS$_2$ (dashed orange).
$r_{\text{Cr-S}} = 2.417(3) \text{ Å}$ and $r_{\text{Cr-Cr}} = 3.543(7) \text{ Å}$ for int-NaCrS$_2$ close to values for bulk O$_3$-NaCrS$_2$ (2.433 and 3.554 Å).[64] Simultaneously, the local structure around Ni resembles the short-range order in fcc-Ni (Figure 6d, R-value 0.010). The Ni-Ni distances of $r_{\text{Ni-Ni}} = 2.480(5)$ Å and $r_{\text{Ni-Ni}} = 3.507(7)$ Å are slightly shorter than in crystalline bulk fcc-Ni (2.492 and 3.524 Å),[70] a phenomenon well known for nanosized particles. Summarizing the findings of pRDF, XANES, PDF, and PXRD experiments, Ni$^{2+}$ ions are extruded from the vacancy layer of the host structure and are reduced to nanocrystalline Ni$^0$ accompanied by formation of int-NaCrS$_2$ (Equation (2), Figure 3a).

During further discharge to 8 Na/NiCr$_2$S$_4$ (region II), peaks corresponding to fcc-Ni display higher relative EXAFS and pRDF amplitudes (Figure S15 and Table S5, Supporting Information) than observed for 2 Na/NiCr$_2$S$_4$. In contrast to the results derived from XANES analyses, no clear evidence for formation of Cr$^0$ is obtained and only one broad signal around 2.04 Å is visible in the pRDF. Utilizing the quick first shell tool in Artemis,[71] assuming a single scattering path for the first shell Cr–Cr separation (corresponding to $r_{\text{Cr-Cr}} = 2.498$ Å)[72] did not result in a reasonable fit indicating the presence of highly disordered ultra-small domains (<1 nm) that are in contact with Na$_3$S, hence assuming a Cr-S scattering path yields a good fit (Figure S15, Supporting Information) with a distance of $r_{\text{Cr-S}} = 2.398(5)$ Å. Such observations are often made for conversion materials due to the amorphous nature of metallic species embedded in a matrix of Na$_2$Q (Q = O, S) acting as transport barrier for the active species. Hence, full reduction of metal ions is suppressed preventing a detailed interpretation, see, e.g., SnO$_2$[73] and FeS$_2$.[74] Taking all findings into account, the full conversion occurring in region I and II is not as simple as described in Equations (1) to (3) and might be better expressed by Equation (4)

$$\text{NiCr}_3\text{S}_4 + (8 - x)\text{Na}^+ + (8 - x)e^- \rightarrow \text{Ni}^2+ + (2 - y)\text{Cr}^0 + \left(4 - \frac{x}{2}\right)\text{Na}_3\text{S} + \text{Cr}_y\text{S}$$

with Cr$_y$S representing a residual X-ray amorphous phase.

Both pRDFs for Cr and Ni of a charged sample in region III (3.0 V, green pRDFs in Figure 6a,b) exhibit only one broad signal corresponding to real space separations of $r_{\text{Cr-S}} = 2.387(5)$ Å and $r_{\text{Ni-S}} = 2.247(8)$ Å (Figure S16, Supporting Information). The latter is shorter than average Ni–S bond lengths, e.g., Ni$_2$S$_2$ (2.27 Å),[75] rhombohedral NiS (2.31 Å),[76] h-NiS$_2$ (2.39 Å),[77] NiS$_2$ (2.40 Å),[78] NiCr$_2$S$_4$ (2.42 Å),[46] whereas the former is in the range for Cr sulfides, e.g., NiCr$_2$S$_4$ (2.39 Å),[46] Cr$_3$S$_4$ (2.42 Å),[79] Cr$_2$S$_3$ (2.42 Å),[79] NaCrS$_2$ (2.44 Å),[64] or CrS (2.46 Å).[80] Summarizing all results: i) distinct sulfide phases could not be assigned in PXRD patterns (compare Figure 4a),
ii) Ni=S and Cr=S bond lengths are affected by the nanoscopic nature of the particles, and iii) the detailed analyses of pRDF and XANES evidence that most of metallic Ni and Cr atoms are oxidized forming a mixture of nanoscopic Ni$_x$S and Cr$_x$S (compare Figure 3a, right). Redox reactions like in Equations (5) to (8) may be assumed for region III

\[ \text{2Cr}^6+3\text{Na}_2\text{S} \rightarrow \text{Cr}_2\text{S}_3 + 6\text{Na}^+ + 6\text{e}^- \]  
\[ \text{3Cr}^6+4\text{Na}_2\text{S} \rightarrow \text{Cr}_2\text{S}_3 + 8\text{Na}^+ + 8\text{e}^- \]  
\[ 3\text{Ni}^6+2\text{Na}_2\text{S} \rightarrow \text{Ni}_2\text{S}_3 + 4\text{Na}^+ + 4\text{e}^- \]  
\[ \text{Ni}^6+\text{Na}_2\text{S} \rightarrow \text{NiS} + 2\text{Na}^+ + 2\text{e}^- \]  

2.4. Cyclic Voltammetry and Electrokinetic Analysis

Results of CV experiments for the third to fifth cycle of Na/NiCr$_2$S$_4$ (see Figure S17 for cycles 1–5, Supporting Information), for the third cycle of Na/Cr$_3$S$_4$ and of Na/NiS are shown in Figure 7a. The third to fifth cathodic CV profiles exhibit two pronounced reduction peaks around 0.75 and 0.42 V (Peaks 1 and 2), whereas two distinct oxidation peaks occur at 1.24 and 1.56 V (Peaks 3 and 4) in the anodic CV curves. For Na/NiS and Na/Cr$_3$S$_4$, only one major reduction and oxidation peak occur together with less distinct features. The Na/NiS CV agrees with literature data [57,81] while no data are available for binary Cr sulfides used in SIBs. The comparison of the CV data recorded for the three different cells does not imply identical Na storage mechanisms, but allows assignment of CV peaks for Na/NiCr$_2$S$_4$ to redox processes involving Ni and Cr as shown in Table 4.

The total stored electric charge $q_{\text{tot}}$ in a CV can be separated into three components: Faradaic contributions from diffusion-controlled redox reactions, Faradaic contributions from the charge-transfer process with surface atoms (pseudocapacitance) [82] and non-Faradaic contributions from the double layer effect, comprehensive explanations are provided in the literature [83–88]. The diffusion-limited redox processes ($k_2v^{1/2}$) and surface capacitive effects ($k_1v$) of an electrode material can be separated by analysis of the electric response $i(V)$ of CV data at various scan rates $v$ according to Equations (9) and (10) [83,89,90]. Values for $b$ in Equation (10) close to 1 imply capacitive effects and close to 0.5 diffusion-controlled processes.

\[ i(V) = k_1v + k_2v^{1/2} \]  
\[ i(V) = \alpha v^b \]  

The electrokinetic analysis of a Na/NiCr$_2$S$_4$ cell is shown in Figure 7b,d. The shapes of CV and GDC curves (compare Figure 2) imply dominating Faradaic electron transfers,

Figure 7. CV analysis in the potential window 3.0–0.1 V: a) CV cycles 3–5 collected for Na/NiCr$_2$S$_4$ (blue), Na/NiS (green, *$i(V)$ scaled by factor 0.3) and Na/Cr$_3$S$_4$ (orange, *$i(V)$ scaled by factor 0.6) cells applying a scan rate of 0.1 mV s$^{-1}$, b) CV curves collected for Na/NiCr$_2$S$_4$ cells applying scan rates between 0.1 and 1.0 mV s$^{-1}$, c) evaluation of $b$ values from linear fits in logarithmic plots of peak currents versus scan rates, and d) quantification of diffusion-limited and capacitive contributions from infinite scan rate evaluation.
especially considering the large peak-to-peak voltage separations of cathodic and anodic events in the CV commonly observed for battery-like materials.[85,88] Peak-to-peak voltage separations distinctly larger than \( \frac{59}{n} \) (\( n \) : number of electrons transferred in the redox process) and the characteristic gradual voltage drift of cathodic and anodic peaks with increasing scan rates indicate quasi-reversibility and enlarged polarization of the NiCr\(_2\)S\(_4\) electrode.[91,92]

The \( b \) values extracted from the logarithmic plot of peak currents versus scan rates (Figure 7c) are closer to 1 indicating high capacitive contributions to the Na storage mechanism. Interestingly, \( b \) values related to the redox pair Ni\(^{2+}\)/Ni\(^{0}\) (\( b_1 = 0.91 \) and \( b_2 = 0.99 \)) are higher than those for the pair Cr\(^{3+}\)/Cr\(^{0}\) (\( b_2 = 0.83 \)). Because the uncompensated Ohmic polarization and quasi-reversible redox reactions limit the total capacity obtained from CV data at high scan rates (compare Figure S18, Supporting Information), the infinite scan rate analysis[93] (see Note S6 and Figure S19, Supporting Information) was conducted using only data recorded for scan rates <0.6 mV s\(^{-1}\).[94–96] The resulting quantitative analysis (Figure 7d) reveals high capacity contributions of 78% applying 0.1 mV s\(^{-1}\) to 90% at 0.6 mV s\(^{-1}\), in agreement with the \( b \) values, which could be explained by the nanosize effect well described in the literature.[86,97] The formation of nanosized domains enhances extrinsic pseudocapacitive contributions and result in beneficial charge storage properties.[97,98] The amorphisation process of NiCr\(_2\)S\(_4\) in the first cycle (compare Section 2.3) results in a predominantly surface-controlled charge storage mechanism with significantly shortened diffusion lengths during subsequent cycling in contrast to the first discharge process, which involves mainly bulk redox reactions.

### Table 4. Results of CV experiments with Na/NiCr\(_2\)S\(_4\) cells after the initial conversion process summarizing redox events, \( b \) values and a comparison to CV data of Na/NiS and Na/Cr\(_3\)S\(_4\) cells.

| Redox event | Na/NiCr\(_2\)S\(_4\) | Redox equation | \( b \) value | Potentials of main CV peaks observed for Na/NiS and Na/Cr\(_3\)S\(_4\) cells |
|-------------|----------------------|----------------|---------------|--------------------------------------------------|
| Reduction   |                      |                 |               | NiS: 0.9 V[57,81]                               |
| 1           | 0.75                 | Ni\(^{2+}\) + 2 e\(^{-}\) → Ni\(^{0}\) | 0.91          | NiS: 0.9 V, this work                           |
| 2           | 0.42                 | Cr\(^{2+}\) + 2 e\(^{-}\) → Cr\(^{0}\) | 0.83          | Cr\(_3\)S\(_4\): 0.44 V, this work              |
| Oxidation   |                      |                 |               | Cr\(^{0}\) → Cr\(^{2+}\) + 2 e\(^{-}\)         |
| 3           | 1.24                 | Cr\(^{0}\) → Cr\(^{3+}\) + 3 e\(^{-}\) | 0.83          | Cr\(_3\)S\(_4\): 1.20 V, this work              |
|             |                      | Cr\(^{0}\) → Cr\(^{3+}\) + 3 e\(^{-}\) |               |                                                   |
| 4           | 1.56                 | Ni\(^{0}\) → Ni\(^{3+}\) + 2 e\(^{-}\) | 0.99          | NiS: 1.6 to 1.7 V[57,81]                        |
|             |                      |                 |               | NiS: 1.66 V, this work                          |

2.5. Results of GITT Measurement

GITT measurements of the first and second cycle (see Figure S20 in the Supporting Information for cycle 1–5, Supporting Information) were performed following the method reported in[99] (Figure 8a). A comparison to a CC test without relaxation steps applying the same current density (multiplied by a factor of 7 in time domain) clearly demonstrates that identical chemical processes occur indicated by a good agreement of electrochemical features. Evaluation of the GITT data allows the estimation of trends and changes of chemical diffusion coefficients.

![Figure 8](https://example.com/figure8.png)

**Figure 8.** a) GITT measurement applying a current pulse of 600 s and relaxation time of 3600 s, compared to a CC test (time multiplied by 7) applying the same current rate; b) alteration of chemical diffusion coefficient and of overpotential (inset) at different potentials (after the current pulses were applied) calculated for the first, second and fifth GITT cycle.
coefficients \( D_{\text{chem}} \) and overpotentials during cycling, although we note that relaxation to total equilibria takes much longer than the applied 3600 s per step. The values of \( D_{\text{chem}} \) (Figure 8b, first, second, and fifth GITT cycle) are smallest during the first discharge (black solid data points in Figure 8b) between 1.0 to 0.8 V (\(3 \times 10^{-12} \text{ cm}^2 \text{s}^{-1}\)) and around 0.25 V (minimum at \( 6 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}\)). Slow chemical diffusion at these stages of discharge result from the corresponding electrochemical processes discussed above: first \( \text{Ni}^{2+}\) extraction and reduction to \( \text{Ni}^{0}\), formation of int-\( \text{NaCrS}_2 \) in region I and subsequently conversion and generation of \( \text{Na}_2\text{S} \) around 0.25 V in region II. The beginning of \( \text{Na} \) insertion in \( \text{NiCr}_2\text{S}_4 \) is accompanied by formation of int-\( \text{NaCrS}_2 \) and avoiding crystallization/deintercalation. Hence, we investigated the long-term investigations after discharge to 0.3 V and charge to 3.0 V (Table S7 and Note S7, Supporting Information) calculated according to Equations (2) and (3) is only \( \geq 37\% \) for 3.0–0.3 V, while \( \approx 18\% \) is estimated for the full conversion. Despite molar volumina being only strictly applicable for crystalline materials, the estimate is a hint that a much lower volume change in the smaller potential window is favorable for cycle stability.

### 2.6. Na Shuttle with Structure Retention during Cycling

Similar to the nickel extrusion mechanism presented in this work, a copper extrusion mechanism was reported for various sulfides like \( \text{CuCr}_2\text{S}_4_{[39,100,101]} \), \( \text{CuTi}_2\text{S}_4_{[82,99]} \), \( \text{CuV}_2\text{S}_4_{[40]} \), and \( \text{CuCrS}_2_{[39]} \) by \( \text{Li} \) or \( \text{Na} \) insertion. In these compounds \( \text{Cu} \) adopts the oxidation state +1, and in the first three compounds charge neutrality is achieved by the presence of valence band holes. Hence, the first electron transferred to the host material fills the hole, and further electrons reduce \( \text{Cu}^{+} \). Here we highlight that uptake of 2 \( \text{Na}^{+} \) ions accompanied by extrusion of 1 \( \text{Ni}^{2+} \) ion from \( \text{NiCr}_2\text{S}_4 \) leads to a high theoretical capacity of 184.2 mAh g\(^{-1}\) compared to host materials based on intercalation/deintercalation. Hence, we investigated the long-term cycling by adjusting the lower cut-off potential to 0.2 V accompanied by formation of int-\( \text{NaCrS}_2 \) and avoiding crystallization of \( \text{Na}_2\text{S} \). The cycle performance test (current rates: 0.5 and 2.0 A g\(^{-1}\), Figure 9a) reveals an outstanding long cycle life with a capacity retention of about 152 mAh g\(^{-1}\) (1.7 Na/\( \text{NiCr}_2\text{S}_4 \)) after 1000 cycles and 88 mAh g\(^{-1}\) (1.0 Na/\( \text{NiCr}_2\text{S}_4 \)) after 3000 cycles. The GDC profiles (Figure S21, Supporting Information) subsequently change, indicating an alteration of electrochemical reactions. PXRD and total-scattering investigations after discharge to 0.3 V and charge to 3.0 V yield very similar results in the 50th compared to the first cycle (Figure 9b.c). After the first discharge reflections of nanosized fcc-Ni and of int-\( \text{NaCrS}_2 \) dominate the PXRD pattern (dark red in Figure 9b), with a position of the (003) reflection of the latter (1.81° 2\( \theta \)) very close to 1.83° 2\( \theta \) of \( \text{O}_3\text{NaCr}_2\text{S}_4_{[37]} \). Charging the electrode leads to significant changes in the PXRD pattern (dark green in Figure 9b): reflections of fcc-Ni disappear and that of \( \text{NiCr}_2\text{S}_4 \) with an astonishingly high crystallinity are present in addition to weak reflections of \( \text{NaF} \) generated during SEI formation (compare Section 2.3) and int-\( \text{NaCrS}_2 \). The (003) reflection of latter shifted to 1.92° 2\( \theta \) indicating the formation of \( \text{Na}_{1-}\text{CrS}_2 \) with a smaller interlayer spacing. Charge compensation for this phase may be similar to that reported for \( \text{Na}^{+} \) deintercalation of \( \text{O}_3\text{NaCr}_2\text{S}_4 \) and \( \text{O}_3\text{NaCr}_2\text{F}_2\text{S}_4_{[37]} \) involving redox of \( \text{S}^{2-} \) anions through formation of electron holes and dimerization to \( \text{S}_2 \) species.[41,42] On the other hand, some residual \( \text{Na}^{2+} \) ions may remain for charge compensation, i.e., \( \text{Na}_{1-}\text{Ni}^{2+}_{1/2}\text{CrS}_2 \), comparable to findings for \( \text{Na/CuCrS}_2_{[39]} \)

The results of the first cycle can be summarized as follows: i) during discharge \( \text{Ni}^{2+} \) cations are removed from the host lattice and are simultaneously reduced, ii) \( \text{Na} \) cations replace \( \text{Ni}^{2+} \) in the vacancy layers and layer-like int-\( \text{NaCrS}_2 \) is generated, iii) during charge \( \text{NiCr}_2\text{S}_4 \) crystallizes, reflections of elemental \( \text{Ni} \) disappear and tiny amounts of \( \text{Na}_{1-}\text{CrS}_2 \) survive. The main differences after the 50th compared to the first cycle are: i) the intensity ratio of the (111) and (200) reflections of \( \text{Ni} \) is reversed after discharge indicating a change of morphology, ii) an increased reflection intensity at 1.92° 2\( \theta \) demonstrates a larger amount of \( \text{Na}_{1-}\text{CrS}_2 \) after charge, iii) reflections of \( \text{NaCr}_2\text{S}_4 \) are broader after charge caused by domain size reduction. The PPDFs (Figure 9c) after the first and 50th cycle exhibit peaks at nearly identical positions with peak positions matching those of \( \text{O}_3\text{NaCr}_2\text{S}_2 \) and fcc-Ni (discharge: Figure 9c, top) or of \( \text{NiCr}_2\text{S}_4 \) (charge: Figure 9c, bottom), respectively. The small crystallite sizes and different capillary packing densities cause deviations on the absolute scale for \( G(t) \) and the intensity ratios. We note that no significant differences are seen for the mid-range order up to 50 Å (Figure S22, Supporting Information). The PXRD and PDF investigations highlight the imperative structural reversibility particularly in the short- to mid-range order during Na shuttle in the reduced voltage range and indicate a reversible nickel extrusion sodium insertion mechanism in region I (compare inset in Figure 9a) described by \( \text{Ni}^{2+} + 2 \text{Na} \leftrightarrow \text{Ni}^{0} + 2 \text{Na}^{+} \). This redox couple intrinsically limits the total amount of transferred charge sacrificing capacity compared to the full conversion (3.0–0.1 V), but gains pronounced cycle stability. The volume change during cycling in both potential windows (Table S7 and Note S7, Supporting Information) calculated according to Equations (2) and (3) is only \( \approx 37\% \) for 3.0–0.3 V, while \( \approx 18\% \) is estimated for the full conversion. Despite molar volumina being only strictly applicable for crystalline materials, the estimate is a hint that a much lower volume change in the smaller potential window is favorable for cycle stability.

### 3. Conclusion

\( \text{NiCr}_2\text{S}_4 \) has a remarkable potential for application as an anode material in SIBs. Our multi-method approach including monitoring structural, electronic and electrokinetic alterations, allowed detailed elucidation of the Na storage mechanism and relations to the electrochemical performance: Full discharge to 0.1 V generates finally fcc-\( \text{Ni}^{0} \) and ultra-small \( \text{Cr}^{0} \) nanoparticles embedded in a nanocrystalline \( \text{Na}_2\text{S} \) matrix and no crystalline products are obtained during charge. As a result, the \( \text{Na}^{+} \) shuttle is predominantly controlled by capacitive contributions and less diffusion-limited, thus boosted by short chemical diffusion lengths yielding an excellent rate capability and high capacity retention, e.g. a superior capacity of 489 mAh g\(^{-1}\) at
2.0 A g\(^{-1}\) in the 500th cycle. Limiting the potential window to 3.0–0.3 V, capacity is sacrificed for the benefit of cycle stability (100 mAh g\(^{-1}\) for 3000 cycles at 2.0 A g\(^{-1}\)) and a compromise in applications must be found whether a long-term stability or large capacity is preferred. Reducing the current density to 0.5 A g\(^{-1}\) delivers a considerably high capacity of 152 mAh g\(^{-1}\) even after the 1200 cycle in the small potential window. The enormous stability can be explained by the unusual reversible nickel extrusion sodium insertion mechanism including highly crystalline phases int-NaCrS\(_2\) and NiCr\(_2\)S\(_4\) (Equation (11))

\[
\text{NiCrS}_2 + 2 \text{Na}^+ + 2e^- \rightleftharpoons 2 \text{NaCrS}_2 + \text{Ni}^0
\]  

(11)

The shuttle of Li\(^+\) between crystalline phases is the basis of commercial LIBs. Here we demonstrated that a similar reaction is possible for SIBs reducing the volume change during cycling compared to full conversion. The difference to electrode materials in LIBs is that Ni plays an important role occupying vacancy layer positions and generating metallic Ni nanoparticles during extrusion, which keeps the crystallites in close contact. The challenge in future work is identifying pseudo-layered materials with reasoned choice of elements and stoichiometry delivering higher capacity in a smaller operating voltage range to move towards application in full cells. Such materials can only be identified understanding charge storage properties, structural and electronic variations as well as the electrokinetic as a prerequisite for advanced battery development. The present study can be regarded as a first step in this direction exploiting layer-like electrode materials in SIBs.

4. Experimental Section

**Synthesis of NiCr\(_2\)S\(_4\):** The pristine material was synthesized via high temperature solid state reaction. Appropriate amounts of nickel (Chempur, 99.99%), chromium (Alfa Aesar, 99%) and sulfur (Chempur, 99.99%) with the stoichiometry NiCr\(_2\)S\(_3.93\) were mixed and ground in a mortar. The slight deficiency of sulfur is necessary for synthesis of a pure material because the phase range of the Cr\(_3\)S\(_4\) structure does not extend to the fully stoichiometric composition as reported.\(^{[45,46]}\) However, for simplification the product was denoted as NiCr\(_2\)S\(_4\) in this study. The mixture was placed in a quartz tube, which was sealed under vacuum (\(<10^{-4} \text{ mbar}\)) and heated at 450 °C for 24 h and subsequently at 1000 °C for 4 days in a furnace before cooling to room temperature. The product
was crushed and mixed in a mortar, pressed into a pellet, annealed at 1000 °C for another 4 days, and again cooled to room temperature.

**Electrochemical Performance Tests:** Electrodes were prepared with 70 wt% NiCr2S4, 20 wt% Super C65 carbon (Timcal), and 10 wt% PVDF (Solvay). All components were suspended in N-methyl-2-pyrrolidone (Fisher Bioreagents, 99.8%) and mixed in a MM400 ball mill (Retsch) for 20 min at 15 Hz. The suspension was spread on carbon coated Cu or Al foil via doctor-blade casting method, dried for at least 24 h at room temperature and subsequently at 60 °C in vacuum for at least 12 h. Swagelok-type test cells were assembled in an argon-filled glovebox using circular electrode disks (d = 10 mm) of the active material (mass-loading of NiCr2S4: 0.6 to 1.5 mg cm⁻²). Na metal as counter electrode, glass fiber filter disks (Whatman) and Celgard membrane as separators. A solution of 1 M sodium trifluoromethanesulfonate NaCF₃SO₃ (Sigma-Aldrich, 98%) in bis(2-methoxyethyl) ether (diglyme, Acros, 99+%, anhydrous) was applied as electrolyte. Galvanostatic measurements were recorded on a BTS 3000 (Neware) battery analyzer applying constant current constant voltage (CCCV) mode. A current density of 0.1 A g⁻¹ (0.14C) was always applied for the first cycle and for the end current of the CCCV mode. C-rates corresponded to an uptake or release of Na uptake/release in Swagelok-type cells at 36.8 mA g⁻¹.

Diglyme and dried for at least 24 h. For PXRD and total-scattering experiments, samples were loaded in 0.7 mm glass capillaries (Hilgenberg, Germany) and sealed with beeswax. For XAS, products were mixed with appropriate amounts of graphite (C-Nergy KS 6 L Graphite, Imerys) in a mortar, pressed into pellets and glued between adhesive Kapton tapes. Samples were transported to the corresponding beamlines in sealed plastic bottles under argon atmosphere.

**High-Energy PXRD and Total-Scattering Experiments:** High-energy PXRD patterns and total-scattering data were collected in Debye–Scherrer geometry at beamline P02.1, PETRA III (DESY, Hamburg) at a wavelength of λ = 0.207 Å (≈60 keV). A Perkin Elmer XRD1621 amorphous silicon area detector was placed at distances of 1000 to 1010 mm (PXRD) and 200 to 350 mm (total scattering). Data processing was performed with DAWN Science.⁵⁰ For calibration and to account for line broadening (PXRD) and dampening (PDF), standard LaB₆ (NIST 660b) was measured applying the same conditions. Rietveld refinements and Pawley fitting were performed using Topas Academic 6.0.⁵⁰ The backgrounds of PXRD patterns were modeled using polynomial background functions. Volume weighted average domain sizes Dᵥ were of coherently scattering domains were extracted by WPPM taking instrumental contribution to line broadening into account applying a Thompson-Cox-Hasting pseudo-Voigt profile. Contributions of glass capillaries, air and Debye scattering to the background were subtracted in figures presenting high-energy PXRD patterns without refinements. Total-scattering data were transformed into atomic PDFs, G(r), applying a Qmax value of 24 Å⁻¹ using xPDFsuite.⁵⁰ An empty capillary was measured under identical conditions to subtract the glass contribution to the PDFs. An example of processing total-scattering Q-space data to r space PDF is shown for representative samples in Figure S23 in the Supporting Information. Ripples particularly visible at r < 2 Å are mainly caused by the finite scattering momentum Qmax applied in the Fourier transform.⁵⁰ Theoretical models were fitted to PDFs using Topas Academic 6.0 taking instrumental parameters as Pseudo-Voigt Q-damping function into account, which was extracted from PDF of LaB₆ (NIST 660b). PDF–PXRD joint refinement was performed applying a weighting scheme such that parts of χ² for both data sets were about equal.⁵⁰ Lattice parameters, atomic positions and DW factors were core-fined during global optimization, in which a spherical PDF peak shape function with lower cut-off was used to contribute for the transition from correlated (small r values) to uncorrelated (high r values) atomic motion. Coordinates of the special crystallographic 2ε Wyckoff position in NiCr2S4 and SOFs of sulfur atoms were fixed during the refinement. Single crystal structure data were used for simulation of reference PXRD patterns and PDFs and as starting crystal data for refinements (NiCr2S4: ICSD 16 884,⁵¹ O3-NaCr2S4: ICSD 42 390,⁶⁴ fcc-Ni: ICSD 52 265,⁵⁰ bcc-Cr: ICSD 44 731,⁷⁰ NaS: ICSD 64 959,⁵⁰ CrS₂: ICSD 16 721,⁷⁰ Cr₂O₃: ICSD 16 722,⁷⁰ CrO₃: ICSD 25 781,¹⁰ NaCrO₂: ICSD 24 595,⁵⁰ FeCr₂S₄: ICSD 625 938,¹¹ h-NiS: ICSD 42 492,⁷⁷ Ni₃S₂: ICSD 654 935).⁶⁵ Graphical visualization of structures was carried out with Vesta ³.⁵⁰

PXRD using Cu Kα₁,₂ Radiation: For some experiments (heating of powder pellets, discharge of PVDF/C65 cell and characterization of reference materials), PXRD was performed using Cu Kα₁,₂ radiation with an Empyreal diffractometer (PANalytical) equipped with an 1D PIXcel detector in Debye–Scherrer geometry.

**X-ray Absorption Experiments:** XAS spectra at the Cr and Ni K-edges were collected in transmission mode at beamline B18, Diamond Light Source, UK. Three spectra of 4 ex situ samples were collected within ~4 min each at both edges using a Si (111) double crystal monochromator. The energy was calibrated to 5989.0 and 8333.0 eV utilizing Cr and Ni reference foils, respectively, between the second and third ionization chamber. Reference XAS spectra of crystalline fcc-Ni foil, bcc-Cr foil and CrS₂, Cr₂S₃, FeCr₂S₄ and h-NiS (synthesis details in Note S8, PXRD in Figure S24, Supporting Information) were measured under identical conditions. The Cr K-edge XAS spectra of O3-NaCr2S4 was recorded at beamline P06, PETRA III (DESY, Hamburg). Two spectra were collected within ~4 min using a Si (111) double crystal monochromator and the energy was calibrated to 5989.0 eV utilizing a Cr reference foil between the second and third ionization chamber. Data processing and linear
combination fitting was realized with Athena and fitting of EXAFS data with Artemis (FEFF6), both implemented in the Demeter 0.9.26 software package. Each spectrum was background corrected, energy-calibrated with respect to the first peak in the derivative spectrum of the reference foils, three spectra were merged, normalized, and the \( k^2 \)-weighted EXAFS \( \chi(k) \) were Fourier transformed (Hanning window, \( k \) range of 3–13 Å\(^{-1} \)) in R space without phase shift correction to obtain pRDFs. Fitting of EXAFS data was performed with theoretical models (NiCr\(_2\)S\(_4\), fcc-Ni, O\(_3\)-NaCr\(_2\)S\(_2\)) derived from crystallographic data including all significant atoms were simultaneously fitted for pristine NiCr\(_2\)S\(_4\). Backgrounds were layered NiCr\(_2\)S\(_4\), sodium insertion, sodium-ion batteries electrokinetics, nickel extrusion, pair distribution function, pseudo-layered NiCr\(_2\)S\(_4\), sodium insertion, sodium-ion batteries.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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[1] B. Dunn, H. Kamath, J.-M. Tarascon, Science 2011, 334, 928.
[2] P. K. Nayak, L. Yang, W. Brehm, P. Adelhelm, Angew. Chem., Int. Ed. 2018, 57, 102.
[3] F. Cheng, J. Liang, Z. Tao, J. Chen, Adv. Mater. 2011, 23, 1695.
[4] H. Zhang, I. Hasa, S. Passerini, Adv. Energy Mater. 2018, 8, 1702582.
[5] M. Hightower, S. A. Pierce, Nature 2008, 452, 285.
[6] M. Armand, J.-M. Tarascon, Nature 2008, 451, 652.
[7] J. B. Goodenough, K.-S. Park, J. Am. Chem. Soc. 2013, 135, 1167.
[8] J. B. Goodenough, Y. Kim, Chem. Mater. 2010, 22, 587.
[9] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, Energy Environ. Sci. 2011, 4, 3243.
[10] J.-M. Tarascon, M. Armand, Nature 2001, 414, 359.
[11] J. Song, B. Xiao, Y. Lin, K. Xu, X. Li, Adv. Energy Mater. 2018, 8, 1703082.
[12] J.-Y. Hwang, S.-T. Myung, Y.-K. Sun, Chem. Soc. Rev. 2017, 46, 3529.
[13] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Chem. Rev. 2014, 114, 11636.
[14] K. He, Y. Zhu, F. Han, Y. Xu, J. Larcher, M. R. Palacín, Energy Environ. Sci. 2011, 4, 3342.
[15] Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cummings, C. Wang, Nat. Commun. 2015, 5, 4033.
[16] Y. Kim, K.-H. Ha, S. M. Oh, K. T. Lee, Chem. - Eur. J. 2014, 20, 11980.
[17] M. D. Slater, D. Kim, E. Lee, C. S. Johnson, Adv. Funct. Mater. 2013, 23, 947.
[18] V. Palomares, S. Ferreras, I. Villalvengua, K. B. Hueso, J. Carretero-González, T. Rojo, Energy Environ. Sci. 2012, 5, 5884.
[19] S. Wenzel, T. Hara, J. Janek, P. Adelhelm, Energy Environ. Sci. 2011, 4, 3342.
[20] Y. Chen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cummings, C. Wang, Nat. Commun. 2014, 5, 4033.
[21] B. Jache, P. Adelhelm, Angew. Chem., Int. Ed. 2014, 53, 10169.
[22] Y. Li, Y. Lu, P. Adelhelm, M.-M. Titirici, Y.-S. Hu, Chem. Soc. Rev. 2019, 48, 4655.
[23] Y. Feng, D. Lan, X. W. Lou, Adv. Mater. 2020, 32, 2002976.
[24] X. Y. Yu, X. W. Lou, Adv. Energy Mater. 2018, 8, 1701592.
[25] Z. Hu, Q. Liu, S.-L. Chou, S.-X. Dou, Adv. Energy Mater. 2017, 7, 1700606.
[26] P. Kulkarni, S. K. Nataraj, R. G. Balakrishna, D. H. Nagaraju, M. V. Reddy, J. Mater. Chem. A 2017, 5, 22040.
[27] Y. Xiao, S. H. Lee, Y.-K. Sun, Adv. Energy Mater. 2016, 7, 1601329.
[28] J. Cabana, L. Conduit, D. Larcher, M. R. Palacin, Adv. Mater. 2010, 22, E170.
[29] F. Klein, B. Jache, A. Bhide, P. Adelhelm, Phys. Chem. Chem. Phys. 2013, 15, 15876.
[30] L. P. Wang, L. Yu, X. Wang, M. Srinivasan, Z. J. Xu, J. Mater. Chem. A 2015, 3, 9353.
[31] P. Liu, J. Han, K. Zhu, Z. Dong, L. Jiao, Adv. Energy Mater. 2020, 10, 2000741.
[32] Z. Zhang, Z. Li, L. Yin, New J. Chem. 2018, 42, 1467.
[33] Y. Cao, L. Xiao, M. L. Sushko, W. Wang, B. Schwenzer, J. Xiao, Z. Nie, L. V. Saraf, Z. Yang, J. Liu, Nano Lett. 2012, 12, 3783.
[34] X. Zhao, Z. Zhang, F. Yang, Y. Fu, Y. Lai, J. Li, RSC Adv. 2015, 5, 31465.
[35] A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon, W. Van Schalkwijk, Nat. Mater. 2005, 4, 366.
[36] Y. Liang, W.-H. Li, Z. Miao, S.-L. Chou, Small 2018, 14, 1702514.
[37] F. Li, Z. Zhou, Small 2018, 14, 1702961.
[38] Q. Wang, C. Zhao, Y. Lu, Y. Li, Y. Zheng, Y. Qi, X. Rong, L. Jiang, X. Qi, Y. Shao, D. Pan, B. Li, Y.-S. Hu, L. Chen, Small 2017, 13, 1701835.
[39] M. Krenkel, A.-L. Hansen, F. Hartmann, J. van Dinter, W. Bensch, Batteries Supercaps 2018, 1, 176.
[40] M. Krenkel, A.-L. Hansen, M. Kaus, S. Indris, N. Wolff, L. Kienle, D. Westfal, W. Bensch, ACS Appl. Mater. Interfaces 2017, 9, 21283.
[41] Z. Shadik, Y.-N. Zhou, L.-L. Chen, Q. Wu, J.-L. Yue, Z. Yang, Q. Wang, X.-Q. Yang, L. Gu, X.-S. Liu, S.-Q. Shi, Z.-W. Fu, Nat. Commun. 2017, 8, 566.
[42] T. Wang, C.-X. Ren, Z. Shadik, J.-L. Yue, M.-H. Cao, J.-N. Zhang, M.-W. Chen, X.-Q. Yang, S.-M. Bak, P. Northrup, P. Liu, X.-S. Liu, Z.-W. Fu, Nat. Commun. 2019, 10, 4458.
[43] B. L. Morris, P. Russo, A. Wold, J. Phys. Chem. Solids 1970, 31, 635.
[44] J. Y. Park, H. M. Ko, W. H. Lee, S. H. Ji, C. S. Kim, J. Appl. Phys. 1993, 73, 5739.
