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Antisite occupation induced single anionic redox chemistry and structural stabilization of layered sodium chromium sulfide

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The intercalation compounds with various electrochemically active or inactive elements in the layered structure have been the subject of increasing interest due to their high capacities, good reversibility, simple structures, and ease of synthesis. However, their reversible intercalation/deintercalation redox chemistries in previous compounds involve a single cationic redox reaction or a cumulative cationic and anionic redox reaction. Here we report an anionic redox chemistry and structural stabilization of layered sodium chromium sulfide. It was discovered that the sulfur in sodium chromium sulfide is electrochemically active, undergoing oxidation/reduction rather than chromium. Significantly, sodium ions can successfully move out and into without changing its lattice parameter c , which is explained in terms of the occurrence of chromium/sodium vacancy antisite during desodiation and sodiation processes. Our present work not only enriches the electrochemistry of layered intercalation compounds, but also extends the scope of investigation on high-capacity electrodes.

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Since the first commercialization in 1991, rechargeable lithium-ion battery (LIB) has powered most consumer electronic devices because of their high gravimetric and volumetric energy densities. LIB has also emerged as a key technology for electric vehicles and has been considered as a good candidate for grid-scale stationary energy storage. Over the past decade, designing and optimizing intercalation cathode materials including the layered oxides (LiMO_2 , NaMO_2), spinel oxides (LiM_2O_4), and olivine phosphates LiMPO_4 (M = transition metals) have contributed greatly in developing new electrode materials for high performance secondary batteries^{1–3}. The fundamental strategy for designing intercalation cathodes used in secondary battery is on the basis of the reversible deintercalation/intercalation of guest ions from/into the host framework without changing the skeleton structure. In general, most of layered intercalation compounds for secondary batteries involve the

cationic reversible redox processes^{4–7}. These compounds, like LiCoO_2 ⁴, NaCrO_2 ⁵, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ⁶, and LiMS_2 ⁷ (M = Ti, V, Cr), can be described as an alternate layer structure with alkali cation sheets sandwiched between transition-metal oxide/sulfide slabs. The transition metal ions as the redox centers could be reduced to a lower oxidation state by electrochemical intercalation of guest ions. Recently, the contributions from anionic redox reactions are reported in high-capacity layered oxides and gaining increasing attentions^{8–12}. Some Li-rich cathode materials, such as $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$ ⁸, $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$ ($0 < y < 1$)⁹, $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$ ($0 \leq y \leq 1$)¹⁰, $\text{Li}_4\text{FeSbO}_6$ ¹¹, and $\text{Li}_2\text{Ir}_{1-x}\text{Sn}_x\text{O}_3$ ($0 < x < 1$)¹², exhibit a cumulative cationic and anionic ($\text{O}^{2-}/\text{O}_2^{2-}$) reversible redox chemistry when Li ions reversibly deintercalate/intercalate from/into these compounds. From both experimental⁸ and theoretical¹³ points of view, recent studies revealed that the anionic redox was triggered by forming

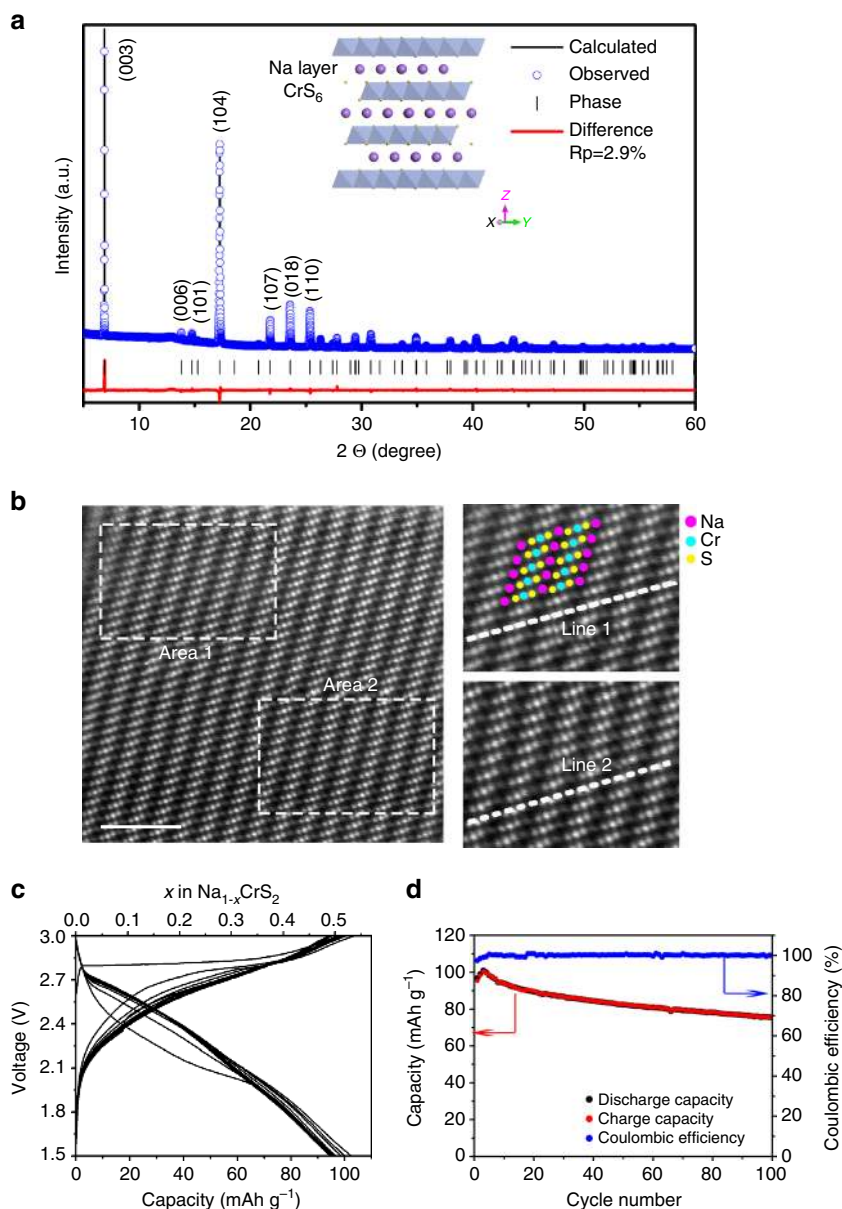


Fig. 1 Structural, morphological, and electrochemical performance of NaCrS_2 . **a** XRD patterns of powder NaCrS_2 (blue circle), calculated profile (black solid line), and their difference (red solid line). Bragg positions are indicated as black vertical tick marks. In the inset for the structure schematic of NaCrS_2 , legend: purple (Na), blue (Cr), and yellow balls (S); **b** HAADF-STEM image of the pristine NaCrS_2 particle, scale bar 2 nm; **c** Galvanostatic charge/discharge curves, **d** cyclic performances and Coulombic efficiencies of NaCrS_2 electrode at 0.5 C

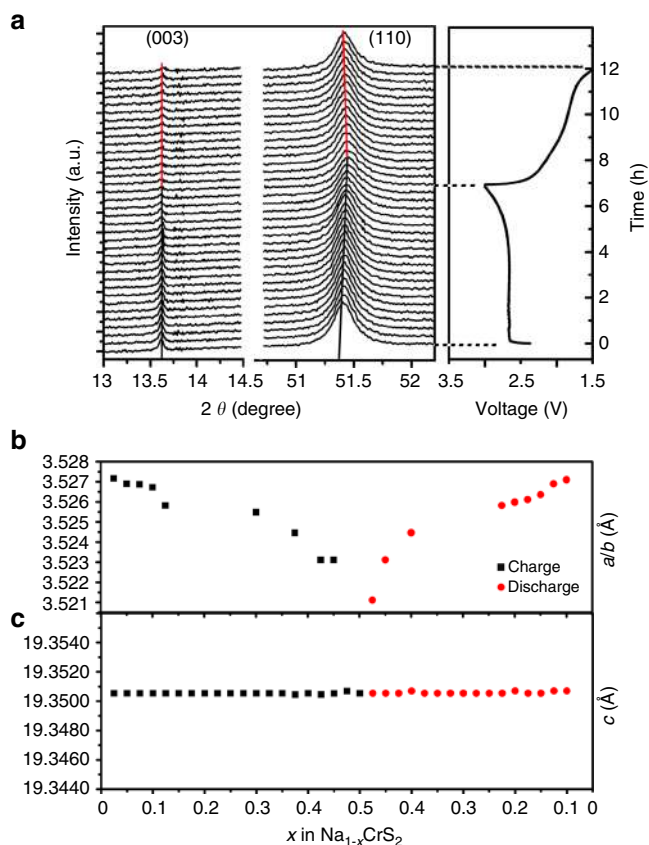


Fig. 2 Structural evolution of NaCrS₂ during sodium deintercalation and intercalation. **a** In situ XRD during the initial cycle for NaCrS₂, corresponding voltage curve is shown on the right. The 2θ is converted to the corresponding angle for $\lambda = 1.54 \text{ \AA}$ (Cu-K α) from the real wavelength $\lambda = 0.7747 \text{ \AA}$ used for synchrotron XRD experiments. Evolution of lattice parameters **b** a/b and **c** c calculated from the in situ XRD during the first charge/discharge process

non-bonding oxygen states, which was created due to that those O 2p orbitals in Li-O-Li configuration have no transition metal orbitals with which it can hybridize. The oxidation of oxygen takes place on the orphaned electrons in Li-O-Li configuration. The increased capacity arises from the fact that two redox bands can be accessed by MO* states and non-bonding oxygen states in Li-rich layer-structured and cation-disordered cathode materials¹⁴. Although this so-called “anion-cation redox competition” behavior was first discussed by Rouxel in 1996¹⁵ with some less-electronegative chalcogenides, the current strategies for designing new high-capacity intercalation-type electrodes are mainly limited to the optimized transition metal redox properties and the utilization of the redox of oxygen. Recently, Du and Goodenough et al.¹⁶ investigated the sole anionic redox in a P3-layered Na_{0.6}(Li_{0.2}Mn_{0.8})O₂, and found that the holes in O-2p bands were introduced during desodiation, but cannot cycle reversibly. Here, a sole reversible anionic redox chemistry of S²⁻/S₂²⁻ is triggered by the Cr/V_{Na} (Na vacancy: V_{Na} in Kröger-Vink notation) antisite, without the redox of transition metal. The relationship between the redox chemistry of S²⁻/S₂²⁻ and its electronic structure is systematically investigated with multi-probe experimental characterizations and theoretical calculations. The motivation of this work is to enrich the reversible redox chemistry of layer-structured intercalation compounds for understanding the nature of their structural and electronic property variations during the deintercalation/intercalation of guest ions.

In this work, the deintercalation/intercalation reaction of NaCrS₂ as a model-layered compound with the typical S²⁻/S₂²⁻ redox is presented. Typical reversible redox chemistry of sulfur, an “abnormal” unit cell breathing behavior and Cr/V_{Na} antisite are observed during the first desodiation/sodiation processes. Density functional theory (DFT) calculations reveal that the top of valence band of NaCrS₂ is mainly populated by S electrons. Therefore, sulfur undergoes redox chemistry for charge compensation during sodium removal. Besides, the occurrence of Cr/V_{Na} antisite triggers the redox of sulfur and is found to be responsible for the “abnormal” unit cell breathing without changing its lattice parameter c .

Results

Structural, morphological, and electrochemical performance.

The crystal structure of NaCrS₂ is measured by synchrotron X-ray diffraction (XRD). The refined pattern is presented in Fig. 1a. All Bragg reflections are indexed by using a rhombohedral symmetry with space group $R\bar{3}m$ (No. 166). This is a typical O3-type layered structure ($a = b = 3.5270(4) \text{ \AA}$, $c = 19.3506(1) \text{ \AA}$) and no crystalline impurities are observed. The crystal structure schematic is illustrated in inset of Fig. 1a. The Rietveld refinement shows reasonable small R factors ($R_p = 2.9\%$, $R_{wp} = 3.9\%$) and high goodness of fit ($GOF (\chi^2) = 4.67$). The structure parameters are listed in Supplementary Table 1. The high intensity ratio (1.55) of (003)/(104) and clearly separated (110) and (018) peaks imply a clear layered O3 structural configuration without Cr/Na antisite defects between the oxygen layers^{17–19}. It is also confirmed by TEM observations at atomic-scale resolution on the pristine NaCrS₂ (Fig. 1b and Supplementary Figs. 1 and 2). Figure 1b exhibits the typical image of high-angle-annular-dark-field (HAADF) for NaCrS₂ sample at atomic-level projected along [100] direction. Line scans are performed on the surface (line 1) and bulk (line 2) of a particle. The corresponding contrast curves from the line scans are presented in Supplementary Fig. 1a, b. The peaks in the curves correspond to Cr, S, and Na atomic columns in the HAADF image. The intensity ratio between Na and Cr column is $\sim 14.59\%$. From STEM images and contrast curves of line scans, it can be concluded that the structural distribution is homogeneous from surface to bulk of the NaCrS₂ particles. NaCrS₂ particles are in irregular shape with a size range of 2–4 μm (Supplementary Fig. 3).

Figure 1c shows the charge and discharge curves of NaCrS₂ at 0.5 C. During the initial charge, NaCrS₂ electrode displays a flat voltage at 2.85 V and delivers a high capacity of 95 mAh g⁻¹ (0.49 Na⁺ per NaCrS₂), which is smaller than that of Na_xVS₂ and Na_xTiS₂ electrodes²⁰ (160 mAh g⁻¹). The initial discharge profile includes a slopy region from 2.8 to 2.1 V and a flat plateau at 2.0 V. The first discharge capacity 92 mAh g⁻¹ is presented. In subsequent three cycles, the charge and discharge capacities gradually increase due to the activation process of electrode, e.g., the specific charge and discharge capacity of 104.1 and 103.4 mAh g⁻¹ is obtained, respectively, in the third cycle. The coulombic efficiency is 99.3%. The cyclic performance and coulombic efficiency of NaCrS₂ electrode are presented in Fig. 1d. The capacity keeps decreasing after the 50 cycles. A capacity of 78.5 mAh g⁻¹ can still be obtained after 100 cycles, whereas the coulombic efficiency increases during the initial 10 cycles and then reaches almost 100% after 100 cycles. At 0.1 C shown in Supplementary Fig. 4, the initial charge capacity is 93.2 mAh g⁻¹. The reversible capacity also increases in a few cycles at the beginning and gets to the maximum value 107.3 mAh g⁻¹, then decreases to 78.6 mAh g⁻¹ at the 100th cycle. The first five cyclic voltammograms of NaCrS₂ electrode are presented in Supplementary Fig. 5. It shows that the cathodic/anodic

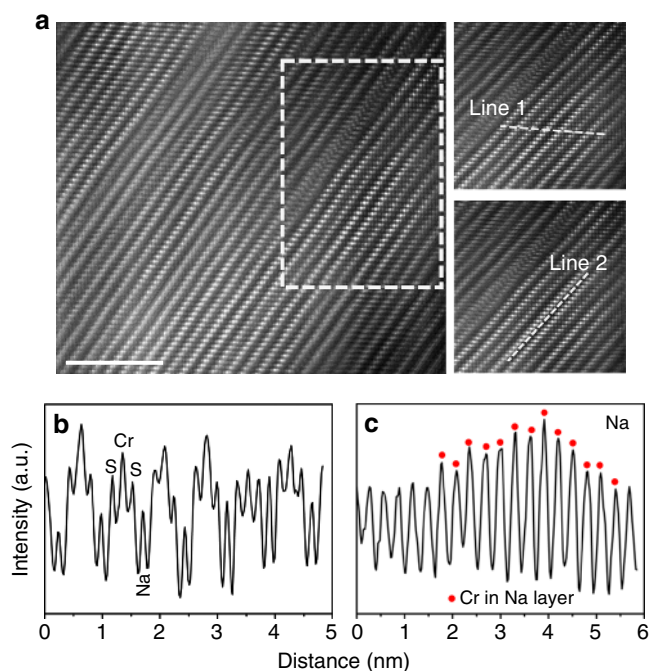


Fig. 3 Atomic structure of NaCrS_2 after charge. **a** HAADF-STEM image of the desodiated particle ($\text{Na}_{1-x}\text{CrS}_2$; $x=0.5$ calculated from capacity), scale bar 5 nm. **b, c** The contrast profiles of the regions scanned by line 1 (Cr, S, and Na ions columns) and 2 (Na columns), respectively. (Red circle represents Cr ion in the Na layer)

peaks emerge at 2.85/2.05 V in the first cycle, which are close to the galvanostatic charge/discharge voltage plateaus in the first cycle in Fig. 1c.

Na-driven structural evolution during cycling. To monitor the structural changes of NaCrS_2 electrode upon sodium deintercalation/intercalation, synchrotron-based in situ XRD is carried out. Figure 2a shows a series of XRD patterns obtained in the initial cycle. In this work, the fully charged state of the $\text{Na}_{1-x}\text{CrS}_2$ electrode is defined by the samples charged to 3.0 V ($\text{Na}_{0.5}\text{CrS}_2$). According to the crystallography theory, (003) and (110) peaks reflect changes along c and a axes of the layered structure, respectively. During the charge process, the (110) peak gradually moves toward higher 2θ angles when x value is increased from 0.0 to 0.5 in $\text{Na}_{1-x}\text{CrS}_2$, indicating a solid solution reaction with the continuous lattice contraction along the a axis. During the discharge process, the (110) peak reversibly moves back to its original position when x value decreases from 0.5 to 0 in $\text{Na}_{1-x}\text{CrS}_2$. Very interestingly, the 2θ angle of (003) diffraction peak keeps unchanged in the entire charge/discharge processes, implying that the lattice parameter c remains almost constant. The lattice parameter evolution of NaCrS_2 electrode during the initial cycle is shown in Fig. 2b, c. From $x=0$ to 0.5 during charge process, the lattice parameter a decreases from 3.527 to 3.521 Å and then reversibly increases back to 3.527 Å during the discharge process. On the contrary, the lattice parameter c keeps unchanged, resulting in a very small unit cell volume change during desodiated/sodiated process. The structure evolution and lattice parameter change of NaCrS_2 electrode during the third cycle are found to be almost consistent with those during the first cycle (Supplementary Fig. 6). No other peak is observed, indicating that no new structure is formed in the subsequent cycles. The invariableness of lattice parameter c of NaCrS_2 electrode during charge/discharge process is quite unusual compared with many

other layered cathode materials, in which the parameter c is mostly increasing during charge and decreasing during discharge known as “normal” unit cell breathing behavior²¹. To our knowledge, the unchanged parameter c was only observed in layered LiNbO_2 system²². In the layered cathodes with “normal” unit cell breathing behavior, the increasing lattice parameter c is due to the expansion of the interlayer spacing caused by the enhanced repulsion force between the two neighboring oxygen layers in delithiation (or desodiation). However, in the LiNbO_2 system, the expansion of the interlayer spacing is compensated by the contraction of the NbO_6 trigonal prism along the c axis because of the deformation of NbO_6 trigonal prism during charge. Because the layered structure of NaCrS_2 with edge-sharing of CrO_6 octahedra is different from that of LiNbO_2 with edge-sharing NbO_6 trigonal prisms, the mechanism of unchanged parameter c in layered LiNbO_2 could not be applied for NaCrS_2 .

In order to understand the “abnormal” unit cell breathing mechanism of NaCrS_2 electrode during the first charge process, the structure of the first charged sample at atomic scale is investigated by STEM. As shown in Fig. 3a, the contrast of Na, Cr, and S atomic columns changes a lot, compared with the pristine sample. The line profiles of Fig. 3b, c are associated with the dash line 1 and 2, respectively. The intensity ratio between Na and Cr column is ~49.81%, which is higher than the ratio in pristine NaCrS_2 sample, implying the existence of cation mismatch. Besides, the intensity fluctuation of Na column confirms the uneven Cr occupation in $\text{Na}_{0.5}\text{CrS}_2$ (red circle represents Cr ion in the Na layer). Similar phenomena have been observed in LiCrO_2 and LiVO_2 electrodes^{23, 24}. Such Cr migration into Na sites may be responsible for the unchanged lattice parameter c .

Detection of Cr valance state. Ex situ Cr K-edge XAS experiments are carried out to examine valance states of Cr during charge and discharge. The red blocks on the curves in Fig. 4a mark the positions for XAS spectrum collection. The X-ray absorption near-edge structure (XANES) spectra of Cr K-edge at various charge/discharge states are presented in Fig. 4b. No obvious change of the spectra is observed during the initial cycle, indicating that very limited redox reaction for Cr ions takes place during the entire electrochemical cycle. This phenomenon is quite different from the other layer-structured cathodes²⁵. The Fourier transformed extended X-ray absorption fine structure (FT-EXAFS) spectra of the pristine and fully charged electrodes are shown in Fig. 4c, d. The first peak at ~2.0 Å is attributed to the single scattering path from the closest S ions to the core Cr ions, and the peak at ~3.25 Å is due to the scattering from the nearest Cr ions in Cr layer. The R values of these peaks are about 0.3–0.4 Å shorter than the real bond lengths, because they are not phase corrected²⁵. Supplementary Table 2 lists the structure parameters derived from fitting. It is observed that the atomic distances of both Cr-S and Cr-Cr are decreasing upon charge, implying the shrinking of Cr-S_6 octahedrons and Cr-Cr_6 hexagons. These are consistent with XRD results showing that the lattice parameter a decreases during the charge process.

EPR spectra. EPR spectroscopy is employed to further monitor the sodium content-induced changes in the oxidation states of Cr or S ions in Na_xCrS_2 series, and Fig. 4f shows the EPR spectra of Na_xCrS_2 series at room temperature (RT). The Cr^{3+} ion in NaCrS_2 has the $3d^3$ electron configuration, which is EPR-active owing to existence of unpaired electrons, while S_2^{4-} in NaCrS_2 is EPR-inactive, because all electrons are paired²⁶. All spectra consist of single Lorentzian line, and g factor is calculated using

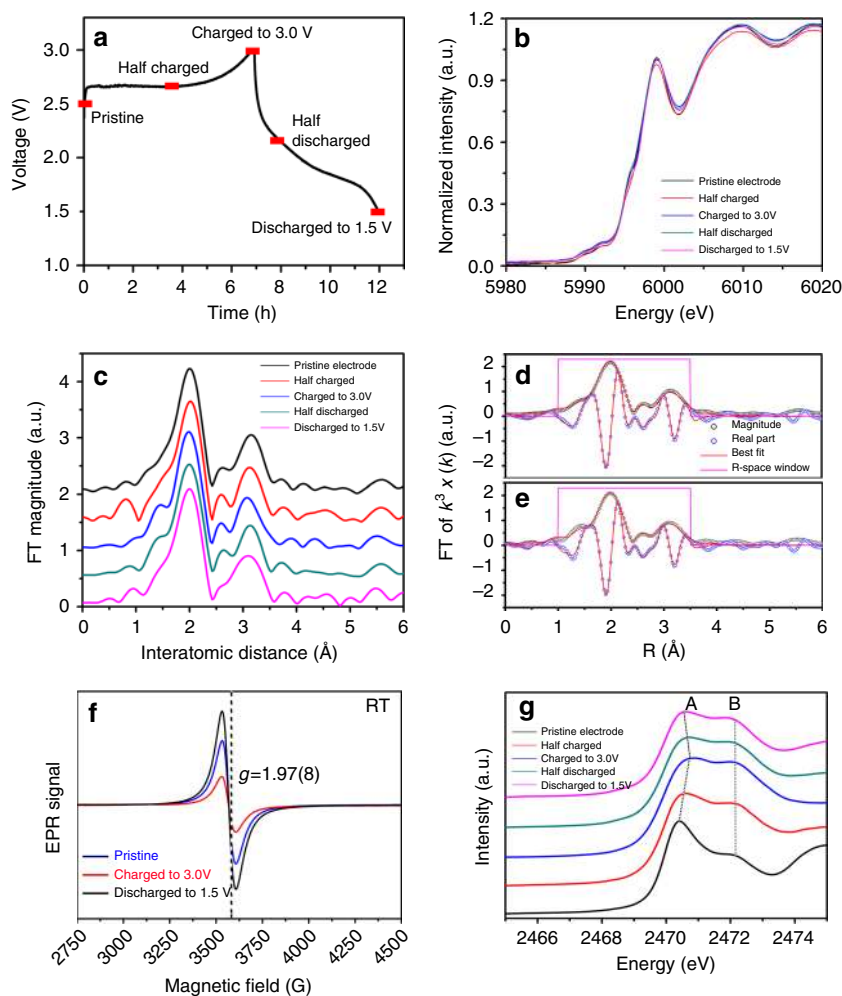


Fig. 4 Detection of Cr and S valence state during various charge-discharge stages. **a** Charge and discharge curves of NaCrS₂ electrode for ex situ XAS. **b** Cr K-edge XANES spectra of NaCrS₂ electrodes at various states. **c** Corresponding FT-EXAFS spectra of the NaCrS₂ electrode at various charge and discharge stages. Calculated (solid red line) and experimental (solid and open circle) FT-EXAFS spectra for **d** pristine and **e** fully charged samples. **f** EPR spectra of pristine NaCrS₂, fully charged and discharged samples recorded at room temperature. **g** S K-edge XANES spectra of NaCrS₂ at the initial cycle

the following relationship²⁷:

$$h\nu_r = g\mu_B H_r. \quad (1)$$

The effective g value of 1.97(8) in the magnetic field of 3570 G obtained from RT is associated with contributions from both exchange-coupled pairs of Cr³⁺^{28, 29}. It is undoubted that the Cr³⁺ EPR-signal and g factor are almost unchanged during charge/discharge processes, indicating the valence state of Cr ions remains unchanged during the first cycle. In addition, no S-signal is detected in the charged sample, which can be explained by the formation of (S₂)²⁻ species that have no unpaired electron as shown in Supplementary Fig. 8, thus are EPR-inactive.

S K-edge XANES. To examine valence states of S for NaCrS₂ during cycling, ex situ S K-edge XANES spectra are measured. As presented in Fig. 4g, two peaks at around 2470.3 and 2472.1 eV in S K-edge XANES spectra of the pristine NaCrS₂ are observed, corresponding to these unoccupied t_{2g} and e_g bands, respectively³⁰. These bands are derived from the hybridization of sulfur 3p states and delocalized Cr 3d states. The peak distance (band splitting of t_{2g} - e_g) about 1.8 eV is close to that of LiTiS₂³¹. In the charge process, the shapes of S K-edge XANES spectra change obviously. A gradually positive shift of the edge peak A to high energy is clearly observed, and there is a large displacement

of about 0.4 eV between the pristine and fully charged states. More interestingly, the intensities of peak B gradually increase during charge. Previous studies reported that a significant increase of the edge peak intensity in S K-edge XANES spectra for lithium deintercalation in Li_xTiS₂ ($0 \leq x \leq 1$) is indicative of the electron transfer involving in sulfur^{31, 32}. The position shifts of peak A and the intensity increments of peak B during charge should mainly result from the contributions of the formation of new chemical bonds to the sulfur atoms. This new peak might emerge around 2742.1 eV and its intensity increases during the charge process. Therefore, such a new peak indicates the oxidation of S²⁻ during the sodium deintercalation process. These variations in S K-edge XANES spectra show reversibility during discharge process, which strongly confirm that the spectral evolution is related to the electrochemical sodium intercalation/deintercalation reactions. From the results above, it can be deduced that charge compensation of NaCrS₂ during charge and discharge is mainly achieved by the redox of S²⁻.

S 2p XPS spectra. To further confirm the electron structure of S during charge and discharge, XPS measurements are carried out on NaCrS₂ at pristine (Fig. 5a), fully charged (Fig. 5b), and fully discharged states (Fig. 5c). For the pristine sample, the S 2p spectra can be deconvoluted into three peaks: two peaks at

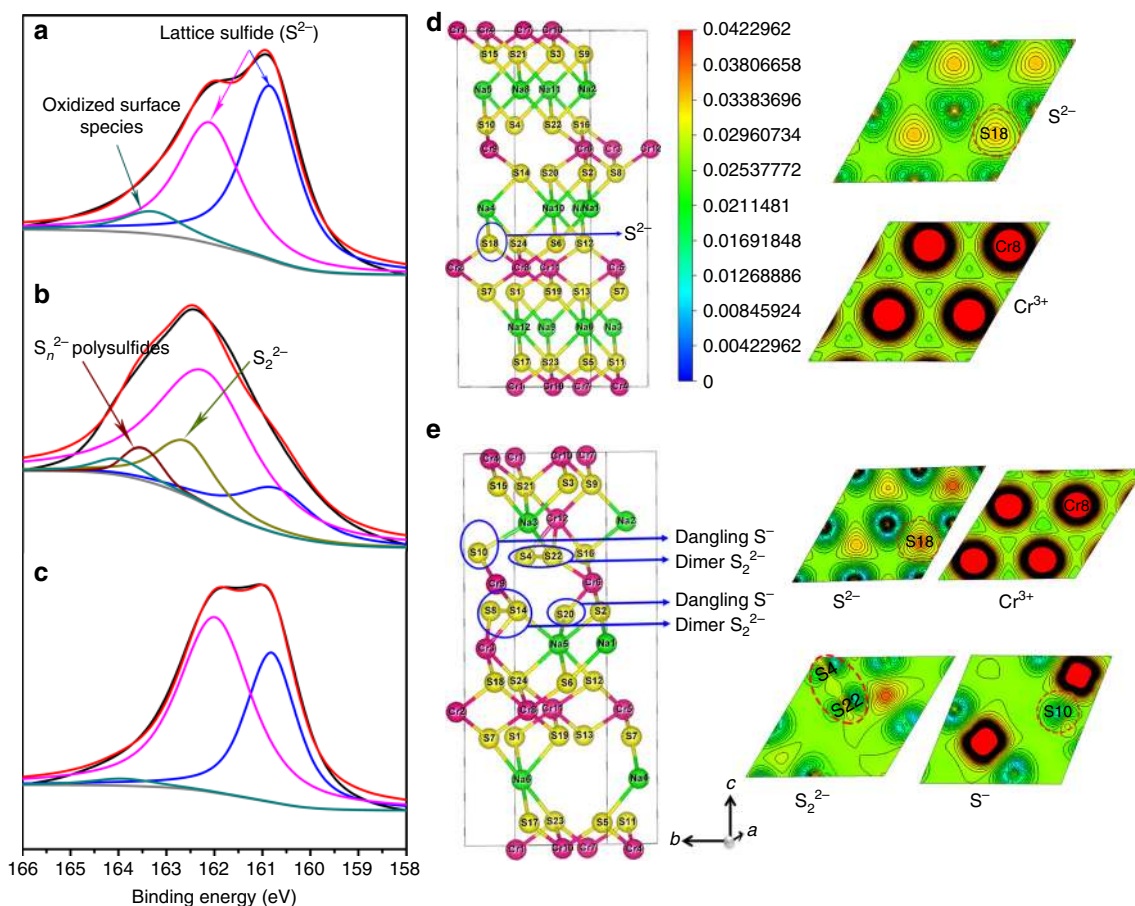


Fig. 5 Detection of S species evolution during various charge-discharge stages. S 2p XPS spectra of NaCrS₂ samples, **a** pristine, **b** after charging to 3.0 V, and **c** after discharging to 1.5 V. Crystal structures and electron density contours of **d** pristine NaCrS₂ and **e** Na_{0.5}CrS₂ with 1/6 Cr/V'_{Na} antisite (2 × 2 × 1 conventional cells). Selected planes are through the Cr and S ions labeled in crystal structures. The contour unit is e/Bohr³ (1 Bohr = 0.529 Å)

160.9 and 162.2 eV are attributable to the lattice sulfide S²⁻, while the peak at 164.0 eV can be explained from certain surface oxidation of species^{33, 34}. After full charge (Fig. 5b), the majority of S²⁻ is oxidized to higher valance states with higher binding energies as expected. The new peaks at 162.6 and 163.6 eV are well assigned to S₂²⁻ and short-chain polysulfides (S_n²⁻, 2 < n < 8)^{35–37}, respectively. After discharge (Fig. 5c), it is obvious that two peaks from S₂²⁻ disappear along with the spectrum shape recovering to that of the initial, further confirming reversible redox of sulfur during charge and discharge processes.

DFT calculations. Figure 6a–c shows the density of states of Cr-3d and S-3p in pristine NaCrS₂. The band gap of 1.27 eV for NaCrS₂ is close to that of 1.16 eV obtained with the atomic sphere approximation³⁸. Furthermore, the calculated magnetic moment of pristine NaCrS₂ (3.322 μ_B) is slightly larger than the experimental value (3 μ_B)³⁸. Figure 6b, c also shows that the vast majority states ranging from –5 to –0.49 eV are occupied by Cr-3d and these states are mainly contributed by t_{2g}, which further confirms that the electron configuration of Cr³⁺ is the t_{2g}³(↑) e_g⁰(↑). Most important is that the majority states from –0.49 to the Fermi level (E_F) and the minority states from –5 eV to E_F originate from S-3p band (See the inset in Fig. 6a). This is in excellent agreement with the angle-resolved photoemission experiment revealing Cr-3d bands below the top of S-3p bands³⁹.

The ground state configuration of Na_{1–x}CrS₂ with different Na concentrations ranging from x = 0 to x = 0.5 are determined by cluster expansion and the results are shown in Supplementary Figs. 9–13. Based on the ground state configuration of Na_{0.5}CrS₂ (without Cr/V'_{Na} antisite) obtained from the cluster expansion and by referring to the XRD and STEM results in Figs. 2 and 3, we build 103 possible configurations with Cr/V'_{Na} antisite (1/6 Cr in the V'_{Na}), whose lattice parameters and total energies are summarized in Fig. 6d–f and Supplementary Tables 3 and 4. As shown in Fig. 6, lattice parameters a' (a': lattice parameter of 2 × 2 × 1 conventional cell, a' is equal to 2a) of all configurations are smaller by 0.02376–0.2297 Å than that of pristine NaCrS₂. Interestingly, a configuration (*red square*) shows a lowest total energy and the c axis length is close to that of pristine NaCrS₂ (19.342 vs. 19.464 Å), but shorter by 1.205 Å than that of Na_{0.5}CrS₂ without Cr/V'_{Na} antisite. Actually, as compared with a sharp increase of lattice parameter c of Na_{1–x}CrS₂ without antisite (from 19.464 Å at x = 0 to 20.622 Å at x = 1/2) as shown in Supplementary Fig. 14, the almost constant lattice parameter c of Na_{1–x}CrS₂ with 1/12 Cr/V'_{Na} antisite is also obtained. Besides, the lattice parameter changes due to the desodiation for NaCrS₂ (Δa = –0.17% and Δc = 0.0%) are much smaller than those for typical layered LiMO₂ family²¹.

We calculate the Na hopping barrier by o–t–o pathway (moving from one octahedral site to an intermediate tetrahedral site, then to another octahedral site) in Na_{0.5}CrS₂ with 1/6 Cr/V'_{Na} antisite. As shown in Supplementary Fig. 16, the calculated Na migration barrier of 0.33 eV is comparable to the typical 1-TM barrier values (~0.3 eV) in layered oxides⁴⁰, indicating the reduced

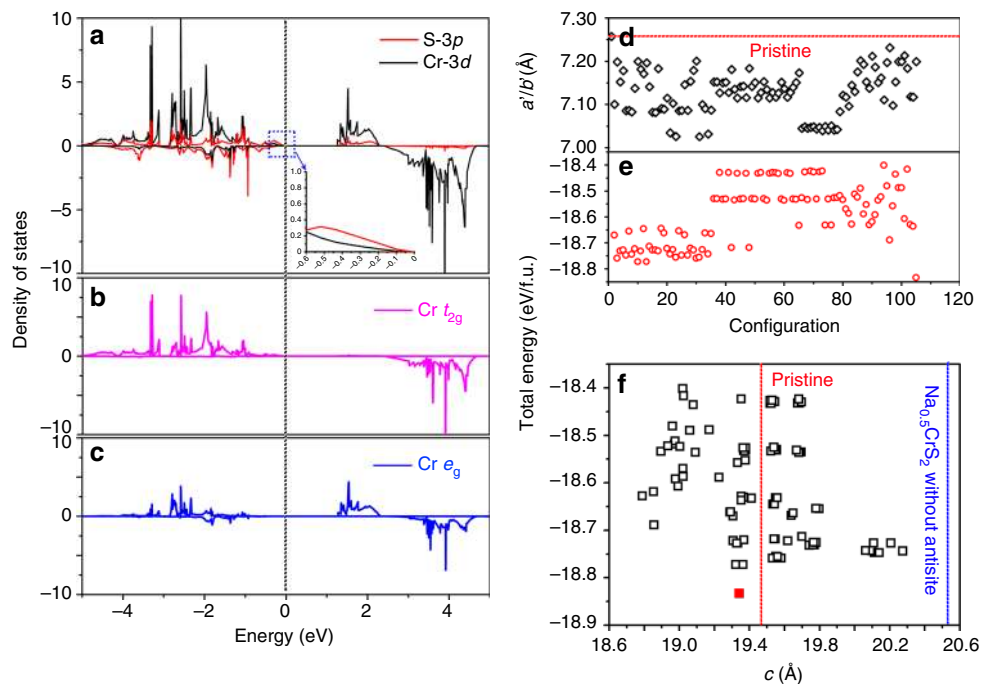


Fig. 6 DOS and Cr/V'Na antisite. **a–c** Density of states of NaCrS₂. **d, e** Calculated lattice parameters a'/b' and total energies of $2 \times 2 \times 1$ conventional cells and **f** dependence of calculated total energy of Na_{0.5}CrS₂ with 1/6 Cr/V'Na antisite on lattice parameter c . The total energy unit is eV/f.u.

tetrahedron height. This result suggests that the Cr/V'Na antisite has the positive effect on Na diffusion. As shown in Supplementary Fig. 17a, along with extraction of Na⁺ from NaCrS₂, Cr first travels to the Na layer via the cross-layer migration, and then realizes the intra-layer migration, which acts as a “glue” between the Cr-S layers. It shortens the interlayer distance, so the length of c axis decreases. Based on XRD, XAS, STEM, and first-principles calculation results, the “abnormal” unit cell breathing of NaCrS₂ upon charge is influenced significantly by cross-layer migration of Cr accompanied by an energy barrier of 0.83 eV (Supplementary Fig. 17b). It is noted that the energy barrier during the electrochemical charge/discharge process should be lower. Such a migration of Cr³⁺ ions can reduce the lattice expansion along the c direction, and then serves as ‘pillar’ to prevent the structure collapse.

In order to further characterize the electronic structure during the desodiation process, we plot the charge densities of pristine NaCrS₂ and Na_{0.5}CrS₂ and 1/6 Cr/V'Na antisite and summarize Cr-S, Na-S, and S-S distances related to all S ions in $2 \times 2 \times 2$ Na_{0.5}CrS₂ with 1/6 Cr/V'Na antisite conventional cell, as shown in Fig. 5d–e and Supplementary Table 5. As compared with NaCrS₂, the charge density distribution of Cr-3d states in Na_{0.5}CrS₂ is nearly unchanged, indicating that Cr ions do not take part in redox reaction during charge/discharge process. Instead, it is found that there are two pairs of dimers S₂²⁻ with an S-S distance of 2.083 Å, two dangling S⁻ ions with two-coordinated Cr ions and others are general S²⁻ ions. It should be emphasized that the usage of the larger-size supercell is expected to give polysulfides ions. The previous XPS and XANES data shown in Figs. 4 and 5 can be well explained by the calculation results.

Discussion

Previous studies on the electrochemistry of sulfur-based electrode materials mainly involve the conversion reaction between two or three species, such as between LiCrS₂ and Cr + Li₂S⁷, between VS₄ and Li₂S + V⁴¹, between CuCr₂S₄ and Cu + Cr₂S₄^{15, 42}, between

Li₂FeS₂ and FeS₂⁴³, and between sulfur and Li₂S⁴⁴. The oxidation of S²⁻ was revealed in some of layered sulfides. For example, the deintercalation of copper from Cu[Cr₂]S₄ with the placement of Cr⁴⁺/Cr³⁺ couples below the top of S-3p state results in the itinerant holes in the S-3p bands. However, copper could not be reversibly intercalated into [Cr₂]S₄¹⁵. Furthermore, the holes in the S-3p bands are not trapped out at S₂²⁻ as discussed by Goodenough⁴². In layered sulfides of LiV_{1-x}M_yS₂ and LiTi_{1-x}M_yS₂ (M = Cr/Fe), the V(IV)/V(III) and Ti(IV)/Ti(III) couples are situated at the top of S-3p states. The holes in S-3p states could also be achieved during lithium removal. However, there are sufficient cation-3d characters from V or Ti enough to prevent the formation of p - p antibonding states. Dahn et al.⁴³ investigated the electrochemical mechanism of Li/FeS₂ and Li/Li₂FeS₂, their results indicated that the deintercalation of Li from Li₂FeS₂ involved Fe³⁺+S²⁻(S₂)^{2-1/2}, in which there is a strong Fe (3d)-S (3p) overlap^{45, 46}. These works indicated the feasibility of inducing the anionic redox by forming the (S₂)ⁿ⁻ species reversibly⁴⁷. On the other hand, previously reported S-based intercalation-type compounds Li_{1-x}CrS₂ only delivered a low capacity of 30 mAh g⁻¹¹⁴². In this work, the reversible discharge capacity of 95 mAh g⁻¹ is presented. The very little change of lattice parameter c and 100% coulombic efficiency during the cycles are quite impressive. By charging up to higher voltages, larger reversible capacities of 120 mAh g⁻¹ can be achieved (Supplementary Fig. 18), and a progressive cationic redox reaction may be involved. Our experimental and DFT calculation results demonstrate that the redox of sulfur is mainly triggered by unique band structure of S-3p of NaCrS₂ and isolated S-3p orbital introduced by Cr/V'Na antisite, and holes in sulfur orbital with a high concentration condense into dianion S₂²⁻.

In layered compounds, a redox couple energy position relative to the top of an anion p band could determine the nature of deintercalation/intercalation reactions. The active TM^{*n*}/TM^{*n*+1} redox couple as a single cationic redox reaction in the layered transition metal compounds, such as LiCoO₂, locates at the top of O²⁻ p band (Supplementary Fig. 19a). The cumulative

Ru (Ir)ⁿ/Ru (Ir)ⁿ⁺¹ and O²⁻/O₂²⁻ redox couples of layered Li₂MO₃^{9, 10} as cationic and anionic redox reactions exhibit a partial overlap at higher potential due to the strong covalent mixing, which can expand the half occupied couple to an itinerant band between Ru (Ir) *d* and O²⁻ *p* bands (Supplementary Fig. 19b). As shown in Fig. 6a, the Cr⁴⁺/Cr³⁺ couple in layered NaCrS₂ is pinned below the S²⁻/S₂²⁻ redox couple, so the empty antibonding states of the redox couple are dominated by S *p* band leading to a single anionic redox reaction. The S₂²⁻/S₂²⁻ couple of NaCrS₂ provides a charge potential of 2.8 V for Na⁺ deintercalation from the octahedral sites if the top of S₂²⁻/S₂²⁻ couple and the pinned Cr 3*d* band are both stabilized by Cr migration into partially occupied Na layer. DFT calculation results indicate that the formation of Cr/V'_{Na} antisite involves three substeps (Supplementary Fig. 17): Cr first travels from Cr site to Na layer via cross-layer migration, and then travels from Na vacancy to another by the distance of 3.446 Å. Finally, via divacancy mechanism, Na migrates from the original lattice site to adjacent vacancy by the distance of 3.629 Å. It means, Cr migration from Na-S-Cr configuration to Na vacancy changes the configuration symmetry around S, resulting in the formation of Na-S-□ (□: Vacancy) configuration. Thus, there will be an isolated S 3*p* orbital, indicating the non-bonding sulfur hole states, which have ionic character rather than covalent character. At a larger concentration, these sulfur holes condense into dianion S₂²⁻ as shown in Fig. 5e. The reaction potential based on the single anionic redox chemistry of S²⁻/S₂²⁻ is relatively low. Nevertheless, its unique features with “abnormal” unit cell breathing behavior (constant *c* axis during charge and discharge) and redox chemistry of S²⁻/S₂²⁻ triggered by Cr/V'_{Na} antisite enrich the in-depth understanding for the nature of redox reaction of layered intercalation compounds. The single anionic redox chemistry of S²⁻/S₂²⁻ may open a new research domain and provide new perspectives on how to design the composition and structure of high-capacity intercalation-type layered metal sulfides for rechargeable batteries by tuning the hybridization of other transition-metal *d* and S 3*p* bands or by designing double anion systems with O and S elements.

Methods

Sample preparation. To synthesize the NaCrS₂ powder materials, a well-grounded mixture of Na₂S, S, and Cr in stoichiometry was placed into carbon-coated quartz tubes. They were heated to 900 °C, kept at that temperature for 6 h, and then cooled down slowly for over 3 h to 300 °C, followed by quenching. All preparation was performed under argon unless otherwise noted.

Electrochemical characterization. A slurry of NaCrS₂ (70 wt%), conductive carbon black (20 wt%), and polyvinylidene fluoride (Sigma-Aldrich, 10 wt%) dispersed in *N*-methyl-2-pyrrolidone (Sigma-Aldrich) was coated on aluminum foil. Two thousand thirty-two coin cells were used for electrochemical test. The electrolyte consisted of 1 M NaClO₄ dissolved in 1:1 (volume) ethylene carbonate/dimethyl carbonate. Electrochemical performance measurements were carried out on a LAND battery tester.

In situ XRD measurements. XRD data were carried out at National Synchrotron Light Source (beamline x14A) at Brookhaven National Laboratory. The wavelength of the X-ray was 0.7747 Å. A home-made electrochemical cell with X-ray windows was used. The angles of XRD spectra were switched to the angles for Cu-Kα ($\lambda = 1.54$ Å), in order to compare with the literature easily.

XAS measurements. Ex situ Cr K-edge XAS spectra were measured at Advanced Photon Source (beamline 12BM) at Argonne National Laboratory. Ex situ S K-edge XAS spectra were obtained at beamline 4B7A in Beijing Synchrotron Radiation Facility. The bending magnet beamline covers the spectral range from 2050 to 5700 eV, with energy resolving power up to 7000 and a beam size of 3 mm × 1 mm. The EXAFS and XANES spectra were processed using Artemis and Athena software packages⁴⁸.

STEM measurements. The detailed measurement set-up was described elsewhere⁴⁹.

XPS characterization. XPS was carried out on a PHI 5000C ESCA System with monochromatic Al-Kα X-ray source. The C 1s peak at 285.0 eV from hydrocarbon contamination was used to calibrate the binding energy.

EPR characterization. EPR spectra were collected on a Bruker EMX-8/2.7 spectrometer. Microwave power was set to 2 mW.

DFT calculations. Based on the projector-augmented wave method within DFT theory⁵⁰, conducted with the VASP program⁵¹, ferromagnetic spin-polarized calculations were carried out. We used the Perdew-Burke-Ernzerhof functional for exchange correlation⁵². We set an effective U_{eff} value to 3.5 eV as discussed in electronic structure calculations on MCrS₂ (M = Li, Na, K, and Ag)⁵³. The plane wave cutoff energy and Monkhorst-Pack *k*-point mesh were set to 550 eV and 2 × 2 × 1 for NaCrS₂ conventional cell, respectively. As for the calculation of the electronic density of states, 4 × 4 × 1 *k*-point mesh for the conventional cell and the modified tetrahedron method were used. The above parameters made the total energy converged to 2 meV per atom. The calculated structural parameters of NaCrS₂ are consistent with experimental ones (*a* and *c*: 3.627582 and 19.446446 Å vs. 3.5270 and 19.3506 Å). To determine the energy barriers for Na or Cr ion diffusion in NaCrS₂, the climbing-image nudged elastic band method⁵⁴ was employed for searching the minimum-energy path.

Data availability. The main data supporting the findings of this study are available within the article and its Supplementary Information files. Extra data are available from the corresponding author upon request.

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Author contributions

Z.-W.F. and S.-Q.S. supervised the research. Z.S., S.-Q.S., and Z.-W.F. wrote the manuscript. Z.S. and J.-L.Y. tested the electrochemical performance. Y.-N.Z. and X.-Q.Y. performed the XRD and XAS measurements. Z.S., J.-L.Y., L.-L.C., Q.W., and S.-Q.S. conducted the DFT calculations. N.Z. and X.L. performed the S K-edge XANES experiments and processed the data. L.G. conducted STEM imaging.


Additional information

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