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Article

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Reversible Dual Anionic-Redox Chemistry in NaCrSSe with Fast Charging Capability

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Abstract: Utilizing the anionic redox reaction opens new approaches for the development of new battery cathode materials with extra capacities. Although, it suffers from several obstacles such as voltage hysteresis and sluggish kinetics. In this paper, a new layered chalcogenide-based on dual anionic-redox reaction is reported. The newly designed layered NaCrSSe exhibits the capacity of almost all Na⁺ intercalation/deintercalation (137 mAh g⁻¹ at 50 mA g⁻¹), and a unique charge/discharge feature with a small polarization of 0.15 V and high energy efficiencies of ~92% in initial cycles. Furthermore, a superior high-rate charge capacity of 115.5mAh g⁻¹ (83.7% retention) was achieved at 27.8 C (4000 mA g⁻¹), which is impressive in all bulk

1 materials for sodium-ion batteries. Systematic characterization studies on structure
2 evolution and DFT calculation show the charge compensation of S and Se anions during
3 cycling. These results will enrich the anion redox chemistry and provide valuable
4 information for developing new anion redox based cathode materials with high capacity
5 and fast kinetics.
6

1 Introduction

2 The intercalation chemistry of layered compounds exhibits a wide variety of
3 charge compensation mechanisms by the oxidation and reduction of transition metal
4 cations, anions or simultaneous cations and anions during the reversible
5 intercalation/deintercalation of the guest ions in the host framework¹⁻⁴. The capacity of
6 electrode materials is closely related to the redox couples during the electrochemical
7 process such as cationic redox ($M^{n+}/M^{(n+1)+}$, where M is a transition metal), or anionic
8 redox ($(2O^{2-}/(O_2)^{n-})$ or $(2S^{2-}/(S_2)^{n-})$). Therefore, high energy density can be achieved
9 through the proper selection of a cation group, or a combination of the cation-anion
10 group. As the traditional multi-cationic-redox-based materials gradually reach the limit
11 of their theoretical capacities, it's becoming more and more necessary to utilize the
12 anionic redox reaction to further enhanced the capacity of reversible ion batteries to
13 satisfy the demand for high-energy-density. For example, the Li-rich material of
14 $Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O_2$ contains three cation redox couples of Ni^{2+}/Ni^{3+} , Ni^{3+}/Ni^{4+} ,
15 and Co^{3+}/Co^{4+} , together with one anionic redox couples of $2O^{2-}/(O_2)^{n-}$ ^{5,6}, which nearly
16 double the capacity of today's $LiCoO_2$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ with the extra
17 contribution from anionic redox reaction. The P2-type compound of
18 $Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$ with Mn^{3+}/Mn^{4+} redox and $2O^{2-}/(O_2)^{n-}$ redox was reported to
19 obtain a capacity of ~ 230 mAh g⁻¹ in Na ion batteries.^{7,8} Also, P2- $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$
20 was reported with anionic redox reaction of O anions and Mn^{3+}/Mn^{4+} redox, delivers
21 the highest energy density (700 Wh kg⁻¹, 270 mAh g⁻¹) among all Na cathode materials.
22 ⁹ However, the widely-studied redox of O anions is likely difficult to break through the
23 bottleneck for practicability, which are mainly voltage hysteresis (low energy efficiency)
24 and sluggish kinetics (low rate capability).^{4,10} While, layered chalcogenides may be the
25 substitution of oxides. Single anionic redox chemistry in layered $NaCrS_2$ was reported
26 not long ago, which undergoes $S_2^{n-}/2S^{2-}$ redox, while the contribution of Cr^{4+}/Cr^{3+} is
27 negligible during the deintercalation/intercalation of Na ions.¹¹ Furthermore, a layered
28 $NaCr_{2/3}Ti_{1/3}S_2$ was successfully developed to fully utilize the synergy effect of the
29 cation (Ti^{3+}/Ti^{4+}) and anion ((S_2^{2-}/S^{n-}) , $(S^{n-}/(S_2)^{n-})$) redox. As expected, the capacity
30 from ~ 100 mAh g⁻¹ in $NaCrS_2$ increased to ~ 190 mAh g⁻¹.¹² Very recently, a Li-rich
31 sulfide $Li_{1.33-2y/3}Ti_{0.67-y/3}Fe_yS_2$ with cationic (Fe^{2+}/Fe^{3+}) and anionic (S_2^{2-}/S^{n-} , $n < 2$) redox
32 processes was reported, which obtained a high capacity of ~ 245 mAh g⁻¹ and undergo
33 comparable low voltage hysteresis and fast kinetics.¹³ These studies advanced the
34 development of new layered compounds with high-energy-density.

35 It is worthwhile to point out: although the utilization of multi-cationic-redox or
36 cation-redox coupled with single-anionic-redox has been widely reported, no similar
37 work on multi-anionic-redox-based layered compounds has been reported for
38 rechargeable ion batteries. Besides, it is well known that cation doping was generally
39 adopted to tune the band structure and property of layered transition metal oxides^{3,14,15}
40 and sulfides^{12,16,17}, the choice of anions is always monotonous, however. As a new
41 approach, in this work, a strategy of anion doping is applied. The reversible dual-
42 anionic-based redox chemistry in $NaCrS_xSe_{1-x}$ is reported for the first time. By
43 introducing the dual anion-redox, the designed $NaCrSSe$ electrode shows a reversible
44 specific capacity of 137 mAh g⁻¹ (96% of the theoretical capacity) with a small

polarization of 0.15 V (no voltage hysteresis), high energy efficiency of ~92% and unapproachable high-rate charge capability (83.7% retention at 27.8C), which is impressive in all bulk materials for sodium-ion batteries, to the best of our knowledge. These superior properties have never been reported in other layered materials based on anionic redox chemistry. In addition, systematic characterization studies and DFT calculation was utilized to study the structure evolution in dual anionic-redox of S and Se, as well as to explain the high-rate charge capability.

Results

Structure of pristine NaCrS_xSe_{2-x}

As shown in Figure 1a-1c, the stack of atom columns of the pristine NaCrSSe sample is observed by STEM. Figure 1a exhibits the image of high-angle annular-dark-field (HAADF) viewed along [110] projection, in which the contrast of the HAADF image varies with an atomic number according to a $Z^{1.7}$ dependency. Cr (Z=24) columns and S/Se (homogeneously mixed, $Z_S=16$; $Z_{Se}=34$; $Z_{average}=25$) columns possess similar high Z-value, hence, they exhibit similarly large contrast, while Na (Z=11) columns with low Z-value show a quite small contrast in HAADF image (see also the red line in Figure 1b). Figure 1c gives the corresponding annular bright-field (ABF) image, note that the ABF images show a $Z^{1/3}$ relationship, therefore, both light and heavy atom columns are visible simultaneously.^{18,19} In ABF image, Na columns are also distinguished clearly (see also the blue line in Figure 1b). The configuration of atom columns displays the O'3-type structure, which is a slightly distorted O3-type structure (Figure S1). The distance of S/Se-Cr-S/Se slabs is measured to be 6.4 Å. It should be noted that a small amount of impurity phase is found (Figure S2).

X-ray diffraction (XRD) spectra of as-prepared NaCrS_xSe_{2-x} powders were measured to further confirm the structure and purity of samples. As shown in Figure S3, XRD patterns of all the prepared NaCrS_xSe_{2-x} ($x=0.5, 1, 1.5$) samples show the O3-type structure. It can be seen that, with the increase of Se ratio, peaks shift to lower degree, and parameters a and c are both elongated (simply derived from distinctive (001) and (104) peaks). As we know, atom size of Se is larger than that of S and the calculated parameters a and c values are 3.632Å and 19.351Å for NaCrS₂ and 3.826Å and 22.447Å for NaCrSe₂, respectively, so it's reasonable that lattice constants of a and c increased as S substituted by Se, leading to the decrease of diffraction 2θ value. The structure and lattice parameters of NaCrSSe is further confirmed by the Rietveld refined results of synchrotron XRD data of NaCrSSe powders as presented in Figure 1d. A distorted O'3-type layered structure (P1) for NaCrSSe and an OP6 model for impurity phase Cr(S/Se)_x are adopted in the Rietveld refinement and the structure parameters are listed in Table S1. The refined lattice parameters of NaCrSSe are a = 3.7683(5) Å, b = 3.6103(6) Å, c = 20.0742(11) Å, α = 90.955(10) °, β = 91.795(8) ° and γ = 118.990(9) °. The low R-factors of $R_p = 6.12\%$, $R_{wp} = 8.98\%$, and $GOF(\chi^2) = 2.15$ obtained for the Rietveld refinement indicates a good fit. Note that c/3 = 6.7 Å, which is attributed to (003) planes, is consistent with the observation of STEM within the margin of error. The small peak at 6.1° in XRD pattern indicates the existence of the impurity phase of Cr(S/Se)_x, and

its weight fraction is calculated to be 5.23% by Rietveld refinement and combining with the coulometry data in electrochemical part below, in which nominal Na content in pristine material is ~ 0.95 per unit, indicating Na vacancy is about 0.05. The accurate composition of the pristine material consists of ~ 0.95 NaCrSSe and ~ 0.05 Cr(S/Se)_x.

A schematic of the O'3 structure corresponding to the STEM images is presented in the inset of Figure 1d, in which S/Se anions make an approximatively ABCABC... stacking, Cr and Na occupy the separating layers of octahedral interspace. As shown in Figure 1e, S4 and S5, EDX analysis proves that the Na, Cr, S, and Se elements are uniformly distributed in all samples, the percentages are measured to be 28.5%: 26.26%: 23.7%: 21.54% (Table S2) for NaCrSSe, which is almost consistent with the NaCrSSe stoichiometry, while the values of NaCrS_{1.5}Se_{0.5} and NaCrS_{0.5}Se_{1.5} also accord with stoichiometry as shown in Table S3 and S4. The pristine NaCrSSe mainly consist of high-density flaky structure with thickness of 2~3 micrometer (Figure S6).

Electrochemistry

The initial galvanostatic charge curves of NaCrS_xSe_(2-x) ($x=0.5, 1, 1.5, 2$) are shown in Figure 2a, while long-cycle curves are exhibited in Figure S7. The first deintercalation Na from NaCrS₂ is characterized by one flat voltage plateaus at 2.8 V and one sloping voltage plateaus from 2.8 to 3.3 V and about 0.46 Na ions per one NaCrS₂ are deintercalated. The voltage plateau of NaCrS_xSe_(2-x) is found to be strongly dependent on the ratio of Se/S because Se is less electronegative than S. A gradually reduce of the flat voltage plateau from 2.8 V to 2.5 V is clearly observed with the increase of Se content in NaCrS_xSe_(2-x). Lowering polarizations should be contributed by the higher conductivity of Se. The voltage platform obtained by DFT calculation are also included for comparison (dash lines in Figure 2a), which is consistent with the experimental data. In addition, the flat voltage plateau becomes longer with the increase of Se content and the sloping voltage plateaus utterly disappears in the charge curves of NaCrSSe and NaCrS_{0.5}Se_{1.5}, implying a different electrochemical reaction from solid solution reaction in NaCrS₂. Among these NaCrS_xSe_(2-x) samples, NaCrSSe delivers the highest charge/discharge capacities as shown in Figure 2b. Therefore, this composition was selected for further investigation. The charge capacity of 138.0 mAh g⁻¹ and discharge capacity of 137.0 mAh g⁻¹ are obtained for NaCrSSe cathode in the first cycle within the voltage range of 1.5-3.3 V at a current density of 50 mA g⁻¹, giving a columbic efficiency of 99.3%. It can be clearly observed from Figure 2b that, NaCrSSe cathode shows charge and discharge flat plateaus at 2.58 V and 2.43 V respectively, with a small polarization of 0.15 V, indicating the feature of two-phase reaction. The Columbic efficiencies keep exceeding 99.7% in subsequent cycles, and the high energy efficiencies more than 90% are achieved in the first five cycles (Figure 2c and S8). The existence of trace inactive impurity ($\sim 5\%$) is responsible for the specific capacity slightly lower than the theoretical capacity (144.1 mAh g⁻¹). Significantly, one Na per NaCrSSe could be extracted, while only 0.46 Na can be extracted from per NaCrS₂. It indicates that extra capacity in Se substituted samples may be attributed to the redox of Se in addition to the S.

Rate performance of NaCrSSe is shown in Figure 2d over a range of current

densities from 50 mA g⁻¹ (0.35C) to 4 A g⁻¹ (27.8 C). At the rate of 3A g⁻¹ (20.8 C) and 4 A g⁻¹ (27.8 C), high charge capacities of 122.4 mAh g⁻¹ (0.85 Na⁺/CrSSe, 88.7% of that at 50 mA/g) and 115.5 mAh g⁻¹ (0.80 Na⁺/CrSSe, 83.7% of that at 50 mA/g) are achieved, respectively. While the discharge capacity of 64.4 mAh g⁻¹ (47.0% of that at 50 mA g⁻¹) is obtained at 4 A g⁻¹. This result indicates that NaCrSSe cathode has super first-class charge rate performance and is able to store charge more than 85% in a 2~3 minutes, which is an impressive rate performance among in all sodium storage layered bulk materials reported previously (Figure S9). Apparently, NaCrSSe does not exhibit the feature of sluggish kinetics for anion redox based materials⁴. Such a fast rate ability for a bulk NaCrSSe cathode material without nanometer-sized, porous structures, carbonaceous hierarchical structures or carbon-coating should be related to superior ion channels with larger lattice parameters and favorable electron-conductivity by introducing of Se.²⁰

In order to clarify the fast kinetics of NaCrSSe, the chemical diffusion coefficient of sodium ions is investigated by Cyclic voltammograms (CV) and Galvanostatic Intermittent Titration Technique (GITT). As shown in Figure 2e, D_{cv} is calculated from the slope of $d(I/A)/dv^{1/2}$, which is $2.67 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for charge (desodiation) process and $1.40 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for discharge (sodiation) process. Na diffusion coefficients obtained by GITT are shown in Figure 2f, which exhibits a U-type variation varied in a large range from 10^{-8} to $10^{-10.5} \text{ cm}^2 \text{ s}^{-1}$. The lowest conductivity of the electrode appears at the middle region for the possible two-phase transition.²¹ Figure 2g exhibits the impedance spectra for a NaCrSSe pellet, the ionic and electron conductivities are calculated to be $1.98 \times 10^{-5} \text{ S cm}^{-1}$ and $1.85 \times 10^{-5} \text{ S cm}^{-1}$, respectively. The value of Na diffusion coefficient is almost the highest one compared with other sodium storage cathode materials as summarized in Table S6.

Structure evolution of NaCrSSe during desodiation

To investigate the structural evolutions of NaCrSSe during Na⁺ deintercalation and reintercalation, a series of *ex-situ* XRD patterns of the electrodes were collected at different states of charge by XRD. As shown in Figure 3a, during the charging process, the intensity of the peaks representing the O'3-NaCrSSe (violet) decrease gradually and finally disappeared at the end of charge (3.3 V). At the meantime, a new phase of O1-CrSSe (green) is formed and the intensities of corresponding peaks keep growing. A higher 2 θ angle of O1-CrSSe (001) peak than that of O'3- NaCrSSe (003) peak indicates a smaller interspace between S/Se-Cr-S/Se slabs. The structure evolution during the discharge process follows the opposite direction of the charge process. The original O'3-NaCrSSe phase can be fully recovered after the completion of first cycle, indicating very good structural reversibility. However, the XRD pattern of NaCrSSe after the 1st cycle shows slightly different features with reduced peak intensity and broadening of (003) and (104) peaks. Similar results were also obtained from synchrotron based XRD data of the pristine, charged and discharged samples as shown in Figure S12. These results indicate a non-crystallization process and reduction of crystallinity of NaCrSSe during the electrochemical process. To obtain clear insight to the local structure evolution of NaCrSSe after electrochemical process, x-ray pair

distribution function analysis (PDF) was utilized. Compared with the XRD technique which uses Bragg scattering only and provides long-range average structural information, the PDF method utilizes both Bragg diffraction and diffuse scattering. Therefore, PDF method can provide local structural information especially the atomic pair distribution, which is related to chemical, structural and morphological information of materials.²²⁻²⁸ PDF of NaCrSSe collected at pristine, charged and discharged state within the long-r range of 0-85 Å are shown in Figure S13. Stronger G(r) peaks are observed clearly from PDF of the pristine sample even at the large atomic pair distance (60-70 Å), indicating the good crystallinity of the pristine sample. However, the intensities of G(r) peaks after charge-discharge cycling reduce significantly, especially at the larger atomic pair distance (>50 Å), indicating that the samples after cycling have poor crystallinity compared with the pristine sample. These results are also supported by the SEM images of the pristine and charged samples as shown in Figure S13 and STEM image of charged sample in Figure S14. S/Se-S/Se van der Waals attraction forces are not sufficient to maintain the layered structure in CrSSe, and the large shrinkage and expansion of c-axis induced the crack formation during the O3 to O1 transformation reaction. Such non-crystallization and crystallinity reduction process during cycling might be responsible for the poor cycle-life and large capacity fade after long cycling (Figure S7 and S8). The layered materials with different chemical compositions and structures such as O2 or P2 by introducing other transition metals such as Al or Ti in layered Na_xCrSSe should be studied to substantially stabilize the phase transformation for the improvement of the electrochemical performance in terms of cyclic stability and efficiency in the future. In addition, NaCrSSe electrode modified by surface coating may be also beneficial to the highly reversible anionic-redox reactions.

Moreover, the coexistence of O'3-NaCrSSe and O1-CrSSe demonstrates a typical two-phase reaction during the charge/discharge process. The DFT calculation (Figure 3b) also reveals that O'3-Na_xCrSSe (0 < x < 1) is not thermodynamically favorable with the positive formation energies of 10~20 meV/f.u., implying the phase separation of O'3-NaCrSSe and O1-CrSSe. This is in good agreement with XRD patterns in Figure 3a.

Atomic-scale resolution STEM observations of charged NaCrSSe were also performed and shown in Figure 3c and 3d. The O1 (P 3 m 1) phase can be observed clearly, in which S/Se anions make an ABAB... stacking and Cr cations occupy octahedral site (insert in Figure 3e). This is similar to the structure of CrSe₂.^{29,30} The distance between the slabs measured in STEM images is 5.4 Å. Rietveld refined synchrotron XRD pattern of charged NaCrSSe is shown in Figure 3e and the refined results are listed in Table S7. It should be noted that impurity Cr(S/Se)_x phase can be observed in charged NaCrSSe Sample. The refined parameters of charged NaCrSSe are $a = b = 3.3861(4) \text{ Å}$ and $c = 5.9637(14) \text{ Å}$, showing about 10% contraction in all three crystal axes comparing with pristine NaCrSSe sample.

Charge compensation and bonding character

Cr K-edge x-ray absorption spectra (XAS): *Ex situ* XAS measurement at Cr K-

edge are carried out to examine valance states of Cr at different charge/discharge states. As shown in Figure 4a, no clear shifts of the Cr K-edge can be observed during charging/discharging process indicating that the contribution of Cr ions in the charge compensation during the electrochemical process is very limited. A small reversible rise/drop in pre-edge should be attributed to the reversible distortion of Cr-S/Se octahedron, allowing the transition of electrons from Cr 1s to Cr 3d- t_{2g} and 3d- e_g , which is forbidden for the undistorted octahedral symmetry.

Se K-edge x-ray absorption spectra (XAS): XAS spectra at Se K-edge at different charge/discharge stages are also measured. As shown in Figure 4b, obvious changes in the Se K-edge XAS spectra can be observed during the charge and discharge processes, indicating the oxidation/reduction of Se. The peak A (red area in Figure 4b) at ~ 12659.6 eV from the transition of 1s electron to unoccupied Cr 3d-Se 4p hybrid orbitals could be assigned to Se^{2-} based on the calibration of FeSe^{31,32,33} (Figure S15a). A shift of peak A to higher energy and the increase of its intensity indicate the oxidization of Se^{2-} upon charging (Figure S15b). Such an increase of intensity can be attributed to the increased population of the unoccupied valence 4p levels caused by the charging process. During discharge process, the shift of peak back to the lower energy and its intensity decreases indicating that the redox of Se ions during the cycling is fully reversible. In addition, the broad peak B at ~ 12670 eV (blue area in Figure 4b) caused by multiple scattering in the coordination sphere³¹ shifts to high energy and its intensity reduces upon charging. It shifts back to the pristine state after fully discharge. All these changes demonstrate that the charge compensation is partly achieved by the redox of Se anions.

S K-edge XAS: XAS spectra at S K-edge at different charge/discharge stages is presented in Figure 4c. The relative intensity of peak A at ~ 2470 eV (red area in Figure 4c) varies greatly during the cycling (Figure S15), and the evolution of peak B at ~ 2480 eV (blue area in Figure 4c) has the similar moving trend as that for Se K-edge. The peak A could be attributed to the transition of 1s electron to the unoccupied Cr 3d-S 3p hybrid orbitals. During the charge process, the emerging and growing of the shoulder peak located at ~ 2468 eV and addition peak formation at 2470.7 eV are clearly observed, corresponding to the formation of the holes of S and the dimerization of S/Se-S/Se respectively¹², and the process reverses upon discharge. These results suggest the reversible valence changes of S anions and the occurrence of $\text{S}^{2-}/\text{S}^{n-}$ and $\text{S}^{2-}/(\text{S}_2)^{m-}$ redox couples during the cycling.

Fourier transformed extended x-ray absorption fine structure (FT-EXAFS): The corresponding FT-EXAFS spectra of Cr, Se and S are also shown in Figure 4d, 4e and 4f respectively. Note that the FT-EXAFS spectra have not been phase-corrected so that the actual bond lengths could be ~ 0.4 Å longer in our case.^{11,34} As shown in Figure 4d, the peak at 2.1 Å of the pristine sample can be attributed to the closest S/Se ions to the core Cr ions, and it shifts to 2.0 Å upon charging. The peak at 2.2 Å in Figure 4e at the pristine state is corresponding to the closest Cr ions to the core Se, which shift to 2.1 Å after fully charging. The peak at 2.1 Å for the pristine state in Figure 4f is corresponding to the closest Cr ions to the core S, which shift to 2.0 Å after fully charging. During charging (desodiation), Cr-S/Se bonds shrink, also shown as the

decrease in lattice parameters “a” and “b” obtained by XRD, caused by the contraction of the S and Se anion radii at higher oxidation states. These structural changes are in line with the mechanism of ‘normal unit cell breathing’.³⁵ During discharge, the changes of Cr-S/Se distances reverse, indicating the reversible evolution of the local structure after sodiation. It should be mentioned that, a small shoulder peak at 1.7 Å in Se FT-EXAFS (Figure 4e) and at 1.6 Å in S FT-EXAFS (non-symmetry of the main peak in Figure 4f) arises after charging, which indicates of the formation of (S/Se)₂^{m-} species.¹²

X-ray pair distribution function (PDF): The structural evolution of NaCrSSe electrode material during the charge and discharge process is also investigated by using X-ray pair distribution function (PDF). As shown in Figure 4g, the first peak at 2.52 Å attributes to the Cr-S/Se bond and the third peak at 3.60 Å attributes to Cr-Cr and S/Se-S/Se bonds. They both shift to low position at 2.44 Å and 3.36 Å respectively upon charging, indicating bond length contraction after the charging process. These agree well with the FT-EXAFS and XRD results. Moreover, the second peak at 2.92 Å related to the Na-S/Se has essentially disappeared upon charge, indicating that the Na ions are almost fully extracted from the structure. Upon discharge, all peaks fully recovered to the pristine states, indicating good reversibility of NaCrSSe cathode.

X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy: Cr 2p, Se 3d and S 2p XPS core peaks of NaCrSSe electrode at different charge/discharge states are shown in Figure 5a-5c. As shown in Figure 5a, the peak of Cr 2p doesn’t change or shift during cycling. Therefore, Cr is considered electrochemically inactive and has almost no contribution for charge compensation. In contrast, Se 3d (Figure 5b) and S 2p (Figure 5c) peaks have significant changes during charging and discharging, further support the conclusion about Se and S are the major contributor for charge compensation obtained by XAS. The details of the peak parameters are listed in Table S8. The shift of major doublet at low binding energy to higher energy upon charging and shift back to lower energy upon discharge indicates the reversible formation of the holes of Seⁿ⁻ and Sⁿ⁻. The binding energy of minor doublet peak evolved from S or Se XPS spectrum at (163.6 eV, 164.8 eV) or (54.6 eV, 55.8 eV) could represent the formation of (S/Se)₂^{m-} dimers according to these previous XPS studies of S₂²⁻ and Se₂²⁻.^{36,37} As well known, XPS is a surface analytical measurement. It should be assumed that the composition from the surface is identical to that from bulk combining with XAS data. Based on the ratio of their areas, it can be estimated that ~1/7 of Se and S dimerize, while the rest ~6/7 anion generate Seⁿ⁻ and Sⁿ⁻ holes upon charging.

Formation of (S/Se)₂^{m-} dimers is also further revealed by the peak formed at 450 cm⁻¹ in Raman spectrum of charged NaCrSSe, it falls in the range of 350-550 cm⁻¹ in Raman spectra from standard compounds with (S/Se)₂ⁿ⁻ species in Figure 5d.³⁸ This result further supports that charge compensation mechanisms of NaCrSSe is partly based on dual anionic-redox process of (S/Se)₂²⁻/(S/Se)₂^{m-}.

Cation migration: The total energy of CrSSe with different amount of Cr migration to the Na site was calculated using DFT and the results are plotted in Figure 5e showing the possibility of antisite formation. The lowest energy occurs at about 25% Cr migration. Such cation migration is directly observed by STEM as shown in Figure

5f. Cr columns can be found between S/Se-Cr-S/Se slabs, which are originally conceived blank. Cation migration to the alkali metal layer upon charging has been reported especially along with anionic redox.³⁹ Cr cation in the vacant layer between the S/Se-Cr-S/Se slabs could be a critical factor to stabilize the structure. Also, antisite can result in the partial dimerization of S/Se due to the generation of suitable unoccupied lone p pairs.

DFT calculation

To confirm dual anion-based (S and Se) redox in theory, the density of states (DOS) is calculated. As shown in Figure 6a, DOS of NaCrSSe reveals an interesting electronic structure in which the S 3p states and the Se 4p states approximately equally dominate in the vicinity of the Fermi level rather than the Cr 3d states. Once NaCrSSe is oxidized, the electron of S 3p states and Se 4p states would be donated in priority. DOS of CrSSe is also calculated (Figure 6b), which shows the dominated occupation of the anions near the Fermi level as well. The S 3p and Se 4p electrons hop beyond the Fermi level, which means these bands are underfilled, corresponding to the conclusion that Se and S donated electron in hybrid orbitals and formed underfilled 3p/4p bands.

As the schematic (Figure 6c) shown, the Se 4p states lay above S 3p states, substituting S partly with Se in layered NaCrS₂ will raise the total valance bands of S/Se anions, and make anions easier to take part in charge compensation. Apparently, the dual anionic redox of S and Se is quite different from those oxygen-redox materials^{4,6,40,41}, in which an A-TM-A (A represents Alkali metal commonly, or Mg⁸, or vacancy⁴²) configuration is formed and the O non-bonding state (orphaned 2p) lying above the stabilized (M–O) bonding band, participates in the redox. While, in NaCrSSe, the p states of S/Se are located above the Cr 3d states in origin state, the Fermi level is pinned at the top of S/Se p states. Hence, a specific configuration or formation of new bands with higher energy are not necessary for the anion redox.

Figure 6d exhibits the numerical charge compensation per atom of NaCrSSe calculate by Bader charge. In NaCrSSe, it donates 0.561 electron per Se atom, and 0.439 electron per S atom during the cycle. As comparison, NaCrS₂ only donates 0.245 electron per S atom. It can be concluded that Se is not only involved in the charge compensation to a great extent, but also activate S to participate more in charge compensation.

The diffusion barrier of Na is calculated and shown in Figure S20. We assumed three intermediate phases – Na_{0.92}CrSSe, Na_{0.5}CrSSe and Na_{0.08}CrSSe between pristine NaCrSSe and full charged CrSSe. It can be concluded that with the decrease of local Na content from 0.92 to 0.08, the diffusion barrier of Na declines from 0.34 eV to 0.19 eV, owing to less Na-Na electrostatic repulsion, which also is contributed to the fast kinetics of NaCrSSe.

Discussions

Utilizing the anion redox can significantly increase the energy density of battery cathode materials. Underlying mechanism of anion redox is also well studied by various

characterization techniques combined with DFT calculation in Li/Na-rich cathode materials. However, several challenges, such as sluggish kinetics and voltage hysteresis at the voltage region of anion redox, irreversible capacity loss in the initial cycle and voltage fade during the subsequent cycles, come relating to anionic redox. In this work, the results of significant improvement on kinetics (fast charging) in layered chalcogenide through S/Se dual anionic doping are reported. As mentioned by J. Rouxel that when the O ligands in layered compounds are replaced by less electronegative anions such as S, Se and Te, the anionic redox process will be enhanced due to the increased overlap of transition-metal(*d*)-anion(*p*) orbitals⁴³. In NaCrSSe, Se has less electronegativity compared with S to provide additional capacity, as well as high electronic conductivity. In addition, introducing Se would enlarge lattice parameters of comparing with sulfides, and may increase the mobility of Na ions.

Based on multi-model characterization and DFT calculations results, trivalent chromium with $d^3(t_{2g}^3(\uparrow) e_g^0(\uparrow))$ electronic configuration in octahedral coordination in NaCrSSe keeps unchanged during desodiation process. The charge composition is predominantly carried out by oxidation of sulfur and selenide during the deintercalation of Na. The dual anionic-redox process is proposed as follows,

Reactions (1) and (2) are fully reversible based on formation of electron holes of S and Se, respectively, which is accompanied by two-phase transformation of O'3- NaCrSSe into O1-CrSSe confirmed by XRD and STEM results. Dual anionic Se and S redox process contribute to 0.561 and 0.439 electron of oxidation respectively according to the DFT calculation. The appearance of the peak at 450 cm^{-1} in Raman spectrum indicates the formation of S/Se–S/Se dimers. The one-seventh of anions estimated from the XPS results further participate in the reversible dimerization of S or Se as shown in reaction (3). The S/Se–S/Se dimers about 1.7 Å could be viewed by S and Se FT-EXAFS. This dimerization reaction should be triggered by the formation of non-coordinated S_{3p} and Se_{4p} orbitals due to the Cr migration to the Na sites in layered structure, which could be investigated by STEM and DFT results. This dual anionic-redox charge compensation mechanism explains the high capacity corresponding to one Na per NaCrSSe in initial charge/discharge process.

The lattice parameter of *c* axis in O'3-NaCrSSe and O3- NaCrS₂ are 20.0742 Å and 19.3506(1) Å, respectively. Apparently, the slab distance of S-Cr-S slabs increases by substituting S partly with Se in O3-NaCrS₂ structure. This undoubtedly provides a more favorable fast channel for ion transport. Na⁺ diffusion coefficients from CV curves is measured to be $2.67 \times 10^{-9} cm^2/s$ for charge process, which is almost superior to all sodium storage bulk materials reported previously (Table S6). The diffusion barrier of Na is as low as 0.19 eV, which is very impressive among the O3 type sodium cathode materials (Table S6). Since the top of Se 4p states lie above S 3p bands, introducing of Se in NaCrSSe is beneficial to the improvement of electron conduction ($\sim 1.85 \times 10^{-5} S cm^{-1}$), and result in the small polarization of 0.15 eV at the rate of 50mA g⁻¹. The discharge voltage of 2.43 V versus Na⁺/Na are assigned to the S^{2-}/S^{n-} and Se^{2-}/Se^{n-}

1 couples by tuning the hybridization of dual anionic Se 4p and S 3p bands. The high
2 columbic efficiency (99.7%) and energy efficiency ($> 90\%$) in the initial cycles and
3 excellent rate capability (the high charge capacities of 115.5 mAh g^{-1} at the rate of 27.8
4 C) could be attributed to the positive effect with dual anionic in NaCrSSe. In addition,
5 NaCrSSe are believed to reduce the chances of releasing S_2 owing to its minimizing the
6 probability of the chemical formation of S_2 as compared to NaCrS_2 . Our results fill the
7 void of multi anionic-redox chemistry in layered compounds for batteries, enrich the
8 intercalation charge compensation chemistry, and guide the design of layered
9 intercalation compounds by new approach. This work, along with the former reports of
10 anionic-redox based layered sulfides, explores a new pathway of layered chalcogenides
11 to solve the practical problem of anionic-redox for high-rate batteries. We expect a
12 combination of multi anionic-redox and traditional multi cationic-redox to design high-
13 performance practical materials in the future.

14 **Methods:**

16 **Material preparation:** Samples of $\text{NaCrS}_x\text{Se}_{(2-x)}$ ($x=0.5, 1$ and 1.5) were prepared by
17 solid-state reactions of stoichiometric amounts of Na_2S (Aladdin, purity:95%), Cr (SCR
18 Co., Ltd, purity:99.95%), S (Alfa Aesar, purity: 99.5%) and Se (aladdin, purity:99.9%).
19 Note that Na_2S , S and Se are excess of 5%. The starting powders were carefully
20 grounded using a mortar and pestle and then pressed into a pellet. The pellet was heated
21 at 900°C for 6 hours in Ar phenomena. After a cooling process, the resulting product
22 was transformed into Ar-filled glove box immediately to avoid contacting with air.

23 **STEM measurement:** The STEM high-angle annular-dark-field (HAADF) and
24 annular bright-field (ABF) images were obtained by a JEM-ARM200F STEM operated
25 at 200 KV and equipped with double aberration-correctors for both probe-forming and
26 imaging lenses. The STEM ABF and HAADF images were taken simultaneously at the
27 optimal defocus value of the HAADF imaging condition, which was more defocused
28 than the optimal ABF imaging condition on this instrument. Thus, the contrast in the
29 ABF image is reversed with the bright area corresponding to the atomic positions. The
30 average background subtraction filter (ABSF) was used to improve the visibility of the
31 images.⁴⁴

32 **Electrochemical characterization:** Electrodes were prepared by a dry coating method
33 in a glove box since $\text{NaCrS}_x\text{Se}_{(2-x)}$ samples are extremely easy to hydrolyze in air and
34 give out a foul smell. Mixture of 80 wt% active material, 10 wt% Super P conductive
35 carbon and 10 wt% polytetrafluoroethylene (PTFE) binder were grounded hardly in a
36 mortar, rolled to thin free standing films and pressed on an aluminum web. For the rate
37 test, electrodes were prepared containing 70 wt% active material, 20 wt% Super P
38 carbon and 10 wt% polytetrafluoroethylene (PTFE) binder, more Super P carbon was
39 added to enhance the conductivity of the electrode. Since the electrodes were made into
40 arbitrary size and shape utilizing PTFE as binder. The mass loading of the electrodes is
41 not strictly consistent. In rate performance experiments, the mass loading is $\sim 8 \text{ mg cm}^{-2}$
42 with weight of $\sim 1.0 \text{ mg}$ (active material $\sim 0.8 \text{ mg}$) and area of $\sim 0.1 \text{ cm}^2$.
43 Electrochemical testing was carried out in 2032 coin cells with a Na metal-disk as the

anode, glass fiber (Whatman GF/F) as separator, and 1 M NaClO₄ dissolved in ethylene carbonate (EC)/ dimethyl carbonate (DMC) (1:1 in volume) with 5 wt% fluoroethylene carbonate (FEC) as the electrolyte. Galvanostatic charge-discharge experiments and GITT (Galvanostatic Intermittent Titration Technique) were carried out on a Land CT2001A battery tester at room temperature. Cyclic voltammograms (CV) and AC impedance test were performed on an electrochemical workstation CHI 660B.

X-ray absorption spectroscopy: XAS of Cr and Se- K edge was measured at beamline 8-ID and 7-BM of National Synchrotron Light Source II (NSLSI-II) in Brookhaven National Laboratory (BNL). The data were collected in the transmission mode. The reference spectrum of Cr metal foil or Se were simultaneously collect during each measurement and used for energy calibration. *Ex-situ* S K-edge XAS spectra were obtained in the fluorescence mode at beamline 4B7A in Beijing Synchrotron Radiation Facility and beamline 9-BM of Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The X-ray absorption near-edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) spectra were processed using the Athena software package.⁴⁵

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Author contribution: Z.-W.F. supervised the whole work. D.-R.S. and Z.-W.F. designed the experiments. D.-R.S. prepared the samples. T.Wang., Z.X., Y.-N.Z. and J.-L.Y performed DFT calculation. D.-R.S., H.-Y.X. and S.-Y.Y. performed electrochemical experiments. D.-R.S. performed lab-XRD and Raman experiments, and conducted XPS experiments. Y.-N.Z. supervised the SEM and EDX characterization work. X.-Y.Y. performed SEM and EDX experiments. L.G. supervised the STEM characterization. Q.-H.Z. performed STEM experiments. L.Z. performed S K-edge XAS data in Beijing Synchrotron Radiation Facility. X.-Q. Y. supervised the characterization work performed at BNL. Z. S. and S.-M. B. performed the Cr and Se XAS data. Z.S. E.H. L.M. and T.Wu. performed the S K-edge XAS data. Z.S, E.H. and

1 S.G. performed the PDF and synchrotron XRD data. Z. S. processed the XAS, XRD
2 and PDF data. D.-R.S. summarized all the data and drew figures. D.-R.S. and Z.-W.F.
3 wrote the manuscript. L.G., L.Z., T.Wang., Z. S. and X.-Q. Y. revised the manuscript.
4

Figure Captions:

Figure 1. Structure of pristine NaCrSSe. (a) HAADF-STEM and (c) ABF-STEM image of the pristine NaCrSSe viewed along [110] projection. (b) Average image intensity profiles of the regions designated by the red line in (a) and its corresponding blue line in (c). (d) Synchrotron XRD patterns of the pristine NaCrSSe powder (red circle), calculated profile (black solid line), and their difference (violet solid line), Bragg positions are indicated as vertical tick marks. (e) EDX analysis of NaCrSSe powder, up: SEM image (scale bar represents 10 μm) and face EDX analysis results, down: corresponding elemental mapping images of Cr (red), Na (blue), Se (violet) and S (green).

Figure 2. Electrochemical performance of NaCrSSe as cathode material for sodium-ion battery. (a) The first galvanostatic charge curves of NaCrS₂ (green), NaCrS_{1.5}Se_{0.5} (cyan), NaCrSSe (black) and NaCrS_{0.5}Se_{1.5} (orange) at a rate of 50 mA g⁻¹, with their calculated voltage platforms (black dash lines). (b) Galvanostatic charge/discharge curves for the first three cycles at a rate of 50 mA g⁻¹. (c) Cycle coulombic and energy efficiencies for the first 5 cycles. (d) Rate capacity at varied current densities. (e) Cyclic voltammograms of the NaCrSSe electrodes for various sweep rates. (f) Na⁺ diffusion coefficients as a function of stoichiometry from GITT. (g) Impedance spectra of a NaCrSSe pellet (mass: 0.4810 g, diameter: 12 mm, thickness: 1.302 mm) at 25 °C, the equivalent circuits used for fitting the impedance spectra is inserted in the figure.

Figure 3. Structure revolution of NaCrSSe. (a) Ex-situ XRD patterns of NaCrSSe at different charge/discharge states in the first cycle, the violet lines represent the patterns of pristine and discharged NaCrSSe and green line represents that of charged CrSSe, their corresponding peaks are also marked by violet and green respectively. (b) DFT calculated formation energies of Na_xCrSSe at different x values. (c) HAADF-STEM, and (d) ABF-STEM image of the charged CrSSe viewed along [110] projection. (e) Synchrotron XRD patterns of the charged NaCrSSe powder (red circle), calculated profile (black solid line), and their difference (violet solid line). Bragg positions are indicated as vertical tick marks, a schematic of CrSSe along [110] projection is inserted in the figure.

Figure 4. Ex situ XAS and xPDF. (a)–(c) Cr, Se and S K-edge XANES spectra of NaCrSSe electrodes at various charge/discharge states which include pristine, half charged (HF, charged to a capacity of 70 mAh g⁻¹), full charged (FC, full charged to 3.3 V), half discharged (HD, discharged to a capacity of 70 mAh g⁻¹ after full charged) and full discharged (FD, full discharged to 1.5 V after full charged). (d)–(f) Corresponding FT-EXAFS spectra of Cr, Se and S. (g) xPDF within a range of 2.0–5.0 Å, the coordination of an S/Se in a NaCrSSe structure showed on the right. The first three peaks are marked with green, violet and yellow dashed line, the corresponding distances are represented with the same color lines in the illustrations on the right.

Figure 5. Dimers and cation migration. (a) Cr 2p, (b) Se 3d and (c) S 2p XPS core peaks of NaCrSSe electrode at different charge/discharge states. (d) Raman spectra of NaCrSSe at different charge/discharge states. The data from FeS₂ and CH₃-S-S-S-CH₃ are included for comparison. The Raman spectrum of CrSe₂ was reproduced from ref³⁸. (e) Calculated total energy of CrSSe with different amount of Cr migration. (f) Color STEM image of charged NaCrSSe (CrSSe). Scale bar refer to 1nm.

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2

3 **Figure 6. The density of states. (a), (b)** Calculated density of states of NaCrSSe and
 4 CrSSe is shown on the right, which is used to represent the charge contribution near the
 5 Fermi level. **(c)** Schematic of density of states. **(d)** The charge compensation per atom
 6 of NaCrSSe (calculated by Bader charges) and NaCrS₂ (ref ¹¹).
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Figures

Figure 1

Structure of pristine NaCrSSe. (a) HAADF-STEM and (c) ABF-STEM image of the pristine NaCrSSe viewed along [110] projection. (b) Average image intensity profiles of the regions designated by the red line in (a) and its corresponding blue line in (c). (d) Synchrotron XRD patterns of the pristine NaCrSSe powder (red circle), calculated profile (black solid line), and their difference (violet solid line), Bragg positions are indicated as vertical tick marks. (e) EDX analysis of NaCrSSe powder, up: SEM image (scale bar represents 10 μm) and face EDX analysis results, down: corresponding elemental mapping images of Cr (red), Na (blue), Se (violet) and S (green).

Figure 2

Electrochemical performance of NaCrSSe as cathode material for sodium-ion battery. (a) The first galvanostatic charge curves of NaCrS₂ (green), NaCrS_{1.5}Se_{0.5} (cyan), NaCrSSe (black) and NaCrS_{0.5}Se_{1.5} (orange) at a rate of 50 mA g⁻¹, with their calculated voltage platforms (black dash lines). (b) Galvanostatic charge/discharge curves for the first three cycles at a rate of 50 mA g⁻¹. (c) Cycle coulombic and energy efficiencies for the first 5 cycles. (d) Rate capacity at varied current densities. (e) Cyclic voltammograms of the NaCrSSe electrodes for various sweep rates. (f) Na⁺ diffusion coefficients as a function of stoichiometry from GITT. (g) Impedance spectra of a NaCrSSe pellet (mass: 0.4810 g, diameter: 12 mm, thickness: 1.302 mm) at 25 °C, the equivalent circuits used for fitting the impedance spectra is inserted in the figure.

Figure 3

Structure revolution of NaCrSSe. (a) Ex-situ XRD patterns of NaCrSSe at different charge/discharge states in the first cycle, the violet lines represent the patterns of pristine and discharged NaCrSSe and green line represents that of charged CrSSe, their corresponding peaks are also marked by violet and green respectively. (b) DFT calculated formation energies of Na_xCrSSe at different x values. (c) HAADF-STEM, and (d) ABF-STEM image of the charged CrSSe viewed along [110] projection. (e) Synchrotron XRD patterns of the charged NaCrSSe powder (red circle), calculated profile (black solid line), and their difference (violet solid line). Bragg positions are indicated as vertical tick marks, a schematic of CrSSe along [110] projection is inserted in the figure.

Figure 4

Ex situ XAS and xPDF. (a)-(c) Cr, Se and S K-edge XANES spectra of NaCrSSe electrodes at various charge/discharge states which include pristine, half charged (HF, charged to a capacity of 70 mAh g⁻¹), full charged (FC, full charged to 3.3 V), half discharged (HD, discharged to a capacity of 70 mAh g⁻¹ after full charged) and full discharged (FD, full discharged to 1.5 V after full charged). (d)-(f) Corresponding FT-EXAFS spectra of Cr, Se and S. (g) xPDF within a range of 2.0-5.0 Å, the coordination of an S/Se in a NaCrSSe structure showed on the right. The first three peaks are marked with green, violet and yellow dashed line, the corresponding distances are represented with the same color lines in the illustrations on the right.

Figure 5

Dimers and cation migration. (a) Cr 2p, (b) Se 3d and (c) S 2p XPS core peaks of NaCrSSe electrode at different charge/discharge states. (d) Raman spectra of NaCrSSe at different charge/discharge states. The data from FeS_2 and $CH_3-S-S-S-CH_3$ are included for comparison. The Raman spectrum of $CrSe_2$ was reproduced from ref38. (e) Calculated total energy of CrSSe with different amount of Cr migration. (f) Color STEM image of charged NaCrSSe (CrSSe). Scale bar refer to 1 nm.

Figure 6

The density of states. (a), (b) Calculated density of states of NaCrSSe and 4 CrSSe is shown on the right, which is used to represent the charge contribution near the 5 Fermi level. (c) Schematic of density of states. (d) The charge compensation per atom 6 of NaCrSSe (calculated by Bader charges) and NaCrS₂ (ref 11).

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